



YEAR XX **Issue 6** / 2026 **ISSN PRINT 1313-0226**
ISSN WEB 1314-507X





MACHINES. TECHNOLOGIES. MATERIALS

INTERNATIONAL SCIENTIFIC JOURNAL

ISSN PRINT 1313-0226, ISSN WEB 1314-507X, YEAR XX, ISSUE 6/ 2026

INTERNATIONAL EDITORIAL BOARD

EDITOR IN CHIEF:

Georgi Popov Technical University of Sofia BG

MEMBERS:

Abdrakhman Naizabekov	Rudny industrial institute	KZ
Ahmet H. Ertas	Bursa Technical University	TR
Albert Albers	Karlsruhe Institut of Technology	DE
Andrzej Golabczak	Lodz University of Technology	PL
Dimitar Karaivanov	University of Chemical Technology and Metallurgy, Sofia	BG
Dobre Runchev	Ss. Cyril and Methodius University in Skopje	NM
Emilia Abadjieva	Akita University	JP
Erdem Camurlu	Akdeniz University, Antalya	TR
Eugen Sheregii	University of Rzeszow	PL
Franz Haas	Graz University of Technology	AT
Galina Nicolcheva	Technical University of Sofia	BG
Gennadii Bagliuk	Institute for Problems of Materials Science NAS of Ukraine, Kiev	UA
Georgii Raab	Ufa State Aviation Technical University	RU
Gregory Gurevich	Shamoon College of Engineering, Ashdod	IL
Hiroiyuki Moriyama	Tokai University, Hiratsuka	JP
Idilia Batchkova	University of Chemical Technology and Metallurgy, Sofia	BG
Iryna Charniak	National Academy of Science, Belarus	BY
Ivan Kralov	Technical University of Sofia	BG
Ivan Kuric	University of Zilina	SK
Iurie Melnic	Technical University of Moldova	MD
Jaroslav Piatkowski	Silesian University of Technology	PL
Julietta Kaleicheva	Technical University of Sofia	BG
Katia Vutova	Institute of Electronics, Bulgarian Academy of Sciences	BG
Maria Nikolova	Angel Kanchev University of Ruse	BG
Natasa Naprstkova	Jan Evangelista Purkyne University in Usti nad Labem	CZ
Nikola Šibalić	University of Montenegro	ME
Oana Dodun	Gheorghe Asachi Technical University of Iasi	RO
Ognyan Andreev	Technical University of Sofia	BG
Predrag Dasic	High Technical Mechanical School of Trstenik	RS
Rasa Kandrotaitė	Kaunas University of Technology	LT
Raul Turmanidze	Georgian Technical University, Tbilisi	GE
Roumen Petrov	Ghent University	BE
Sergey Dobatkin	National University of Science and Technology "MISIS", Moscow	RU
Souren Mitra	Jadavpur University, Kolkata	IN
Svetlana Gubenko	National Metallurgical Academy of Ukraine, Dnipro	UA
Vedran Mrzljak	University of Rijeka	HR
Wu Kaiming	Wuhan University of Science and Technology	CN

TECHNICAL EDITORS:

M. Sc. Eng. Radoslav Daskalov,
M. Sc. Eng. Oleg Mihailov

All articles are published after peer review by two independent reviewers.

Scientific and technical union of mechanical engineering
108 R. S. Rakovski str., Sofia, Bulgaria
www.stumejournals.com, office@stumejournals.com

CONTENTS

MACHINES

Rapid prototyping of a friction coupling for joining rebar

Nikola Šibalić, Marko Mumović 210

TECHNOLOGIES

Complex-composition ceramics based on Al₂O₃ and basalt glass

Marek I., Dudnik O., Bagliuk G., Diduk I., Red'ko V., Koval O., Mosina T. 214

Tolerance treatment of sliding pairs and repeatability in assembly

Štefan Václav, Jozef Peterka 217

Influence of thermodynamic properties of metallic materials on the efficiency of hydro-vacuum atomization and hydriding processes

David Sakhvadze, Gigo Jandieri, Besik Saralidze, Georgi Sakhvadze, Anzor Kupharadze, Nata Sulakvelidze, Zivzivadze Onise 220

Study of the influence of the cross-linker on the modification of cotton fabric with chitosan for controlled release of diclofenac and preparation of antimicrobial textiles

Daniela Atanasova 229

Integrated comparative assessment of material, energy and construction-time efficiency of prefabricated and conventional reinforced concrete systems

Veis Šerifi, Nazim Manić, Emir Maslak, Vesnera Šerifi 232

MATERIALS

Intelligent Brazing Materials

Emilia Florina Binchiciu, Ionelia Voiculescu, Florin Catalin Tabacu, Ioan Binchiciu 239

Innovative Nanomaterials for the Conservation and Sustainable Protection of Cultural Heritage

Iskra Tsvetanska, Ivanka Yankova, Kamelia Nucheva 242

Thermodynamic Properties and Phase Equilibria in the Fe–W–C System

Vladyslav Kaverynskyi., Stepan Kyryliuk, Gennadii Bagliuk, Yevheniia Kyryliuk, Volodymyr Kudin, Larysa Romanova, Valentyna Sudavtsova 245

Rapid prototyping of a friction coupling for joining rebar

Nikola Šibalić^{1*}, Marko Mumović¹

Faculty of Mechanical Engineering, University of Montenegro, Podgorica, Montenegro¹
nikola@ucg.ac.me

Abstract: Friction couplings for joining rebar are widely used in civil engineering and mechanical structures, including the construction of high-rise buildings, towers, bridges, overpasses, tunnels, dams, and other infrastructure. These friction couplings are mechanical elements that provide a strong and reliable connection between the components being joined by transferring loads through the friction force generated between the contact surfaces. This force is applied by the geometry of the friction coupling and the installation-induced clamping force. The primary factor governing the proper selection and application of a friction coupling is the cross-sectional diameter of the rebar, as the friction coupling must be designed to withstand the loads encountered under service conditions. In addition, environmental influences, particularly the difference in the coefficients of thermal expansion of the joined materials, represent an important consideration. Another critical factor is the installation process itself, as the performance of the friction coupling depends directly on proper installation. Therefore, comprehensive testing of the installed friction coupling is essential to ensure its reliable performance throughout its service life. This paper presents an original design solution for the development of a friction coupling for joining Ø25 mm rebar, developed through three successive design iterations. The proposed friction coupling is intended to ensure structural integrity under static and dynamic loading, including seismic loading and vibration. An initial prototype design was developed in accordance with the applicable technical standards and validated using the Finite Element Method (FEM) to evaluate its load-bearing capacity under static loading conditions and identify potential stress concentrations. The prototype models were manufactured using the Fused Filament Fabrication (FFF) additive manufacturing process with the support of CAD/CAE systems. The friction coupling was ergonomically designed through mass and shape optimization.

KEYWORDS: FRICTION COUPLING, REBAR, CAD/CAE, ASSEMBLY, RAPID PROTOTYPING

1. Introduction

Rapid prototyping encompasses a set of techniques used to quickly produce physical models, enabling fast and cost-effective evaluation of a product's geometry and functionality without the use of complex tooling, most commonly through additive manufacturing technologies [1, 2]. The resulting prototype may be fully functional if its intended application is not particularly demanding. More frequently, however, prototypes are only partially functional because the materials used do not possess the properties required for full operational performance. Such prototypes are particularly useful for experimental investigations focused on geometric evaluation [3], for which a variety of file formats are available [4]. The application of this approach significantly reduces both product development time and manufacturing costs [5]. In this study, the rapid prototyping approach is applied to the development of a friction coupling for joining rebar.

Reinforced concrete is the most widely used construction material due to its high compressive strength; however, it exhibits relatively low tensile strength. This limitation is overcome by incorporating rebar, which also improves several other mechanical properties of the material. For easier transportation and handling, rebar is manufactured in standardized lengths, which are often insufficient for practical construction applications requiring longer reinforcing bars. One of the major challenges in civil engineering is to provide a reliable method for joining rebar, particularly for larger diameters, without compromising the structural integrity of reinforced concrete. Accordingly, the objective of this research is the development of a friction coupling for joining rebar in reinforced concrete structures. Couplings are widely used in civil engineering and mechanical structures, including the construction of high-rise buildings, towers, bridges, overpasses, tunnels, dams, and other infrastructure. These couplings are mechanical elements that provide a strong and reliable joint between the components being joined by transferring loads through the friction force generated between the contact surfaces. This force is produced by the geometry of the friction coupling and the installation-induced clamping force.

The primary factor governing the proper selection and application of a friction coupling is the cross-sectional diameter of the rebar, as the friction coupling must be designed to withstand the loads encountered under service conditions. In addition, environmental influences, particularly the difference in the coefficients of thermal expansion of the joined materials, represent an important consideration. A third important factor is the installation process itself, as the performance of the friction coupling depends directly on proper installation.

2. Prototype development

The friction coupling is designed as an assembly consisting of internally toothed jaws specifically adapted to the rebar profile and external tapered sleeves that provide the clamping action.

The rebar sections to be joined pass through the jaws. After the jaws and external tapered sleeves have been assembled, a compressive installation force is applied to produce a permanent joint by satisfying the self-locking condition. To achieve self-locking of the tapered connection, an appropriate selection of material, geometric parameters, and the surface finish of the tapered contact surfaces is required to satisfy the condition:

$$\operatorname{tg} \frac{\alpha}{2} \leq \mu \quad (1)$$

Where $\alpha/2$ is the half cone angle and μ is the coefficient of friction. This operating principle enables the friction coupling to be used with a wide range of rebar diameters and profiles.

The components are assembled on-site after the rebar has been positioned. Once installed, the friction coupling is intended to carry axial tensile loads. The principal performance characteristics of the friction coupling are its tensile load capacity and elongation, which are evaluated through tensile testing.

The initial prototype of the friction coupling for joining rebar is shown in Figure 1.

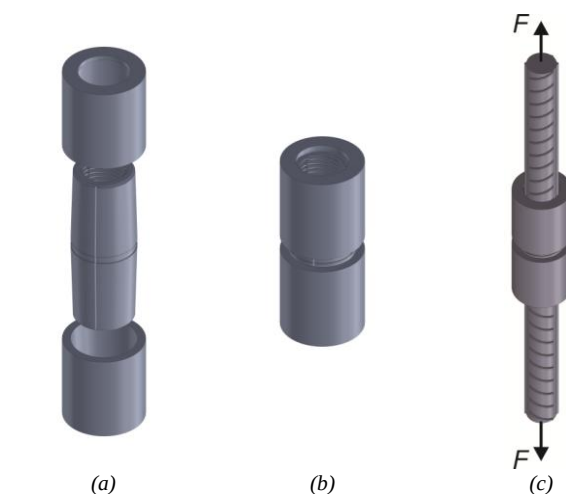


Fig. 1 Friction coupling for joining rebar
(a) Exploded view of the friction coupling; (b) Assembled friction coupling; (c) Friction coupling installed on rebar

The initial prototype was manufactured using the Fused Filament Fabrication (FFF) additive manufacturing process and is shown in Fig. 2.

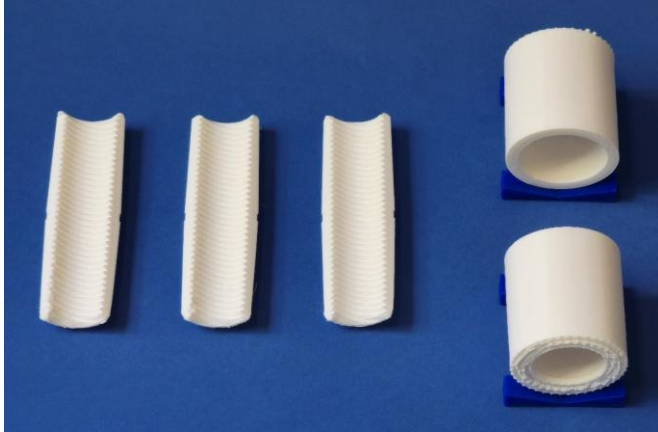


Fig. 2 First iteration of the friction coupling prototype

The main challenge arises at the contact interface between the jaws and the rebar, as the surface of the rebar exhibits complex geometry with a wide range of rib profiles and dimensional tolerances. To address this issue, the jaws of the friction coupling were designed with multi-start, large-pitch helical grooves intended to engage with the ribs of the rebar. In the first design iteration, these helical grooves were unidirectional. However, it was observed that they could not adequately accommodate rebar manufactured in different production batches, primarily because of variations in the orientation of the ribs. Therefore, in the second design iteration, the helical grooves were improved by incorporating overlapping grooves in both directions. The resulting design, shown in Fig. 3, provided significantly better conformity between the friction coupling and the rebar than the first iteration.

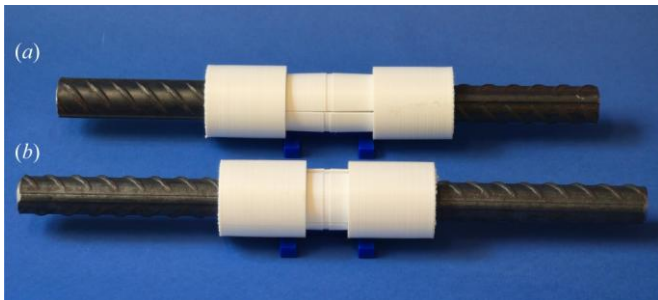


Fig. 3 Comparison of the friction coupling prototype assembly
(a) First iteration; (b) Second iteration

The second challenge was the application of the installation force under on-site conditions. To address this issue, a threaded connection was introduced between the upper and lower external tapered sleeves. This design modification enables the operator to perform the assembly and tightening procedure on-site using standard hand tools in a simple and practical manner. All three iterations of the friction coupling prototype are shown in Fig. 4.

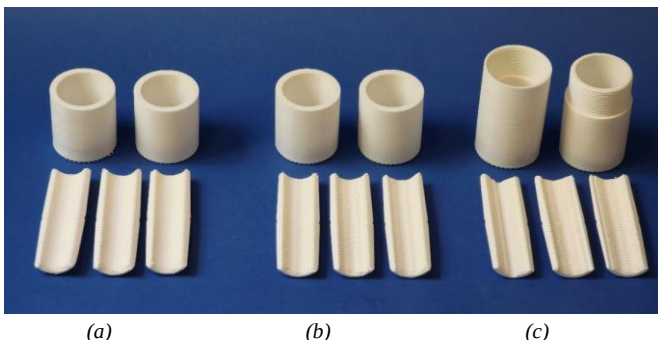


Fig. 4 Components of the three friction coupling prototype iterations
a) First iteration; (b) Second iteration; (c) Third iteration

To generate the preload force in the friction coupling, the threaded connection on the external tapered sleeves must be tightened. In order to achieve the required clamping force of $F_p = 15 \text{ kN}$, a tightening torque T_p must be applied to the specified M45 thread with a 2 mm pitch. The required tightening torque is calculated using the following equation [6]:

$$T_p = F_p \cdot \frac{d_2}{2} \cdot \tan(\varphi + \rho_n) \quad (2)$$

Where: $d_2 = 43.701 \text{ mm}$ is the pitch diameter of the thread, $\varphi = 0.83^\circ$ is the thread helix angle, $\rho_n = 13^\circ$ is the friction angle, and the tightening torque calculated using the equation above $T_p = 80.75 \text{ Nm}$.

3. Numerical simulation of the prototype

The friction coupling prototype developed in the third design iteration and manufactured from modeling materials proved to be operational. Before manufacturing a fully functional prototype from the selected metallic materials using modern CNC machining technologies, it is advisable to evaluate the CAD model in a CAE environment in order to identify potential design deficiencies.

This analysis was carried out in the *Static Structural* module of Ansys, which is based on the Finite Element Method (FEM). Since the ribs on the surface of rebar are manufactured in a wide range of profiles and dimensional tolerances according to ISO 6935-2:2019 [7], and because the interaction between the rebar ribs and the toothed jaws is highly nonlinear, these contact surfaces were approximated as smooth. Furthermore, since the preload is generated through the threaded connection of the external tapered sleeves, the threads were also simplified by representing their effect as an equivalent axial preload force.

The primary operating mechanism of the friction coupling is friction. Therefore, neglecting the interlocking effect between the rebar ribs and the toothed jaws reduces the load-carrying capacity of the coupling, representing a conservative loading scenario that may also occur in practice. The simplified geometry of the prototype is shown in Fig. 5.

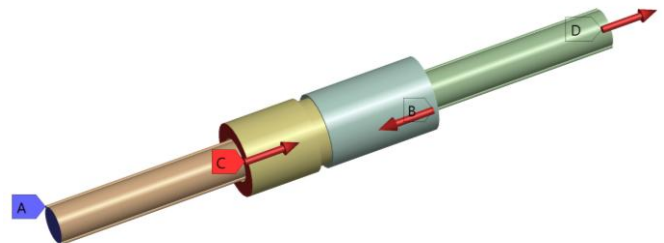


Fig. 5 Simplified geometry of the third prototype iteration with mechanical boundary conditions

One end of the rebar was defined as a *fixed support* and is denoted by A (Fig. 5). The clamping forces responsible for preloading the friction coupling were applied to the surfaces of the external tapered sleeves. These forces, denoted by B and C (Fig. 5), were each assigned a magnitude of 15 kN. To evaluate the performance of the friction coupling, the opposite end of the rebar was subjected to a tensile force, denoted by D (Fig. 5), with a magnitude of 246 kN. This value corresponds to the tensile strength of the selected Ø25 mm rebar multiplied by its cross-sectional area. This load was selected as the test load because a successful friction coupling design should withstand it without significant relative displacement of the rebar within the coupling. Under these conditions, failure is expected to occur by fracture of the rebar rather than by slippage from the friction coupling. The contacts between the surfaces in contact with the rebar were defined as frictional, with a coefficient of friction of 0.5 [8], which is representative of non-machined steel surfaces or surfaces exposed

to corrosion. The relatively high coefficient of friction partially compensates for the neglected interlocking effect between the rebar ribs and the toothed jaws.

To realistically represent the operating principle of the friction coupling, the simulation was divided into two stages. During the first stage, the friction coupling was preloaded by clamping the rebar. Only forces *B* and *C* were active, increasing continuously from zero to their final values over a period of 1 s. The stress distribution in the friction coupling at several time instants during the first stage is shown in Fig. 6.

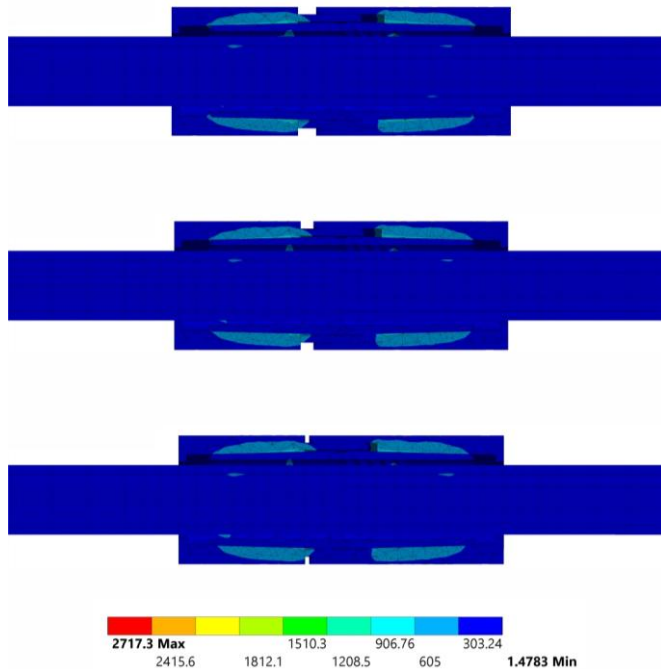


Fig. 6 Stress distribution in the friction coupling (MPa) during the first stage of the simulation at three time instants

The total deformation analysis indicates that the largest displacement occurs in the external sleeves, which is consistent with the intended operating principle of the proposed design (Fig. 7).

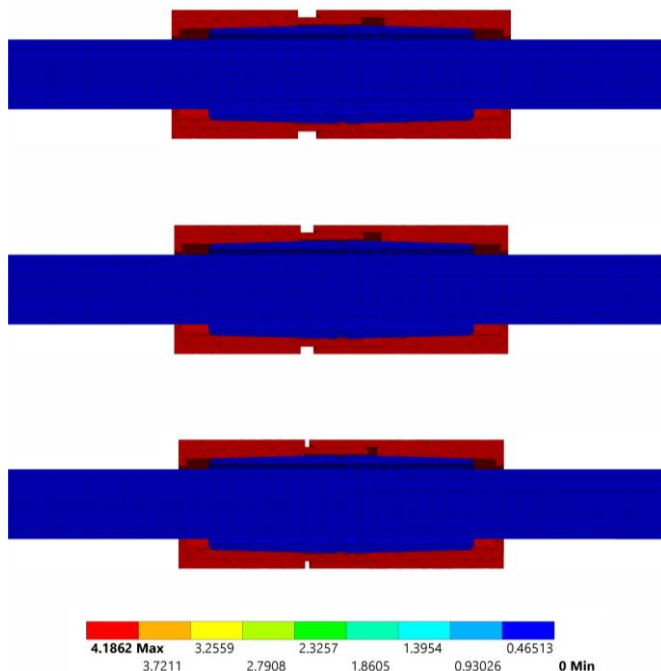


Fig. 7 Total deformation of the friction coupling (mm) during the first stage of the simulation at three time instants

Total deformation represents the magnitude of the displacement of a point (node) from its original position due to the applied loads, boundary conditions, contact interactions, and other influencing factors.

During the second stage of the simulation, forces *B* and *C* remained constant at their previously established values, while the tensile force *D* was applied continuously between 1 s and 2 s, reaching its maximum value at the end of this interval. The stress distribution in the friction coupling at half of the applied tensile load and at the maximum load is shown in Fig. 8.

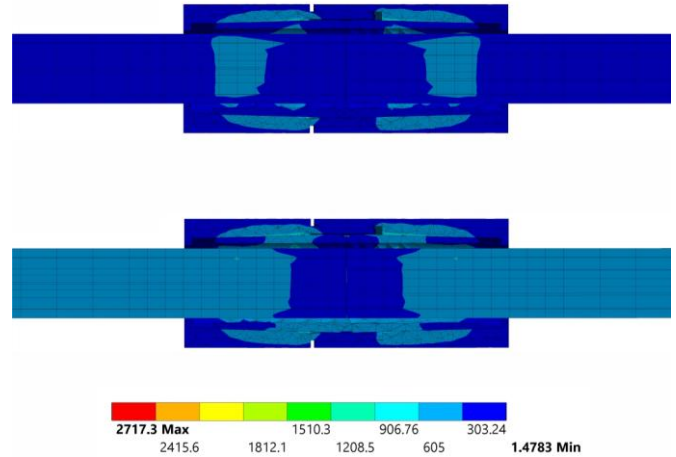


Fig. 8 Stress distribution in the friction coupling (MPa) during the second stage of the simulation at 50% of the applied tensile load and after reaching the maximum tensile load

The total deformation results indicate a slight displacement of the external tapered sleeves caused by elastic deformation, i.e., the elongation of the internal sleeve (Fig. 9).

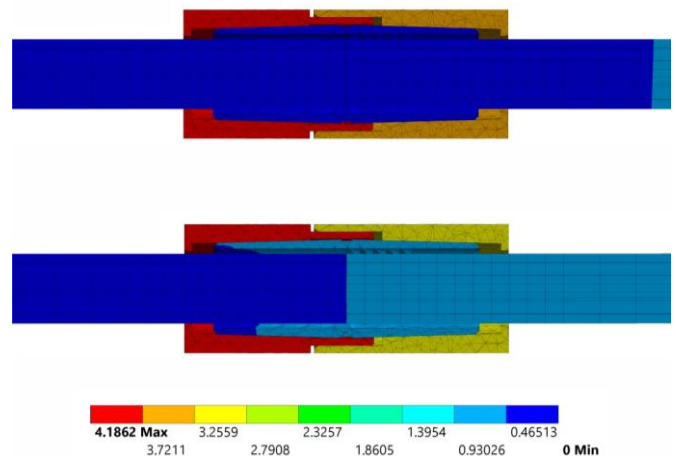


Fig. 9 Total deformation of the friction coupling (mm) during the second stage of the simulation at 50% of the applied tensile load and after reaching the maximum tensile load

To monitor the displacement of the rebar under the applied tensile force *D*, a *Deformation Probe* was defined on the end surface of the rebar located inside the friction coupling. The results indicate a displacement of 0.61 mm under the action of force *D*, which is considered acceptable.

4. Conclusion

The developed prototype, based on the design iterations presented in this study, is intended for use in civil engineering applications involving the joining of rebar. The main limitation of the initial design was related to the contact interface between the jaws and the rebar, which was successfully addressed by introducing a double-start helical groove. The second limitation

concerned the practical application of the installation force and was resolved by incorporating a threaded connection between the upper and lower external tapered sleeves. Proper installation is achieved by applying a tightening torque of $T_p = 80.75 \text{ Nm}$.

By applying the Rapid Prototyping Method, all identified design flaws were eliminated within a short development period, and in three iterations operational solution was obtained of the friction coupling. The third prototype iteration was evaluated using FEM analysis. The numerical simulation was performed in two stages. The first stage represented the installation and preloading process, while the second stage simulated the application of tensile load up to the tensile strength of the selected rebar material. Under the maximum applied load, the simulation predicted a relative displacement of the rebar with respect to the friction coupling of 0.61 mm, which is considered acceptable.

The next step of this research will involve manufacturing a fully functional prototype and conducting experimental testing under laboratory conditions. The prototype will be evaluated by determining its tensile strength and percentage elongation as indicators of joint quality. The developed friction coupling should satisfy the required performance criteria by transferring the mechanical properties of the base material, in this case Ø25 mm rebar.

The developed prototype represents a practical and innovative solution for joining rebar in a wide range of civil engineering applications. Its simple installation procedure and minimal influence on the integrity of the reinforced concrete cross-section make it a promising alternative for future construction projects, with significant potential for practical implementation.

Acknowledgement

This paper is the result of project POC-008-25 received from the Innovation Fund of Montenegro and the University of Montenegro - Faculty of Mechanical Engineering as part of the Proof of Concept Program

Literature

- [1] T. A. Yesiwas, A. B. Tiruneh, and M. A. Sisay, "A review article on the assessment of additive manufacturing", 2025.
- [2] H. I. Medellín-Castillo and J. E. P. Torres, "Rapid prototyping and manufacturing: A review of current technologies," *ASME Int. Mech. Eng. Congr. Expo. Proc.*, vol. 4, no. February, pp. 609–621, 2010, doi: 10.1115/IMECE2009-11750.
- [3] Steve Upcraft and Richard Fletcher, "The rapid prototyping technologies," *Assem. Autom.*, vol. 23, no. 4, pp. 318–330, 2003.
- [4] T. S. Jones and R. C. Richey, "Rapid prototyping methodology in action: A developmental study," *Educ. Technol. Res. Dev.*, vol. 48, no. 2, pp. 63–80, 2000, doi: 10.1007/BF02313401.
- [5] M. Šibalić, N. Šibalić, M. Šekularac, and A. Vujović, "Process of Rapid Prototyping Using Wind Turbine as an Object of Experimental Research," *Lect. Notes Networks Syst.*, vol. 472 LNNS, pp. 220–226, 2022, doi: 10.1007/978-3-031-05230-9_25.
- [6] R. Bulatović, "Mašinski elementi I", Podgorica: Univerzitet Crne Gore, 2016, ISBN: 978-9940-527-15-0
- [7] ISO 6935-2:2019, Steel for the reinforcement of concrete - Part 2: Ribbed bars, Published (Edition 4), 2019.
- [8] R.J.M. Pijpers and H.M. Slot, "Friction coefficients for steel to steel contact surfaces in air and seawater", *Journal of Physics Conference Series* 1669(1):012002, 2020, DOI: 10.1088/1742-6596/1669/1/012002

Complex-composition ceramics based on Al_2O_3 and basalt glass

Marek I., Dudnik O., Bagliuk G., Diduk I., Red'ko V., Koval O., Mosina T.

Institute for Problems of Materials Science National Academy of Science of Ukraine, Kyiv, Ukraine

i.marek@ipms.kyiv.ua, o.dudnik@ipms.kyiv.ua, g.bagliuk@ipms.kyiv.ua, i.diduk@ipms.kyiv.ua, v.redko@ipms.kyiv.ua,

o.koval@ipms.kyiv.ua, t.mosina@ipms.kyiv.ua

Abstract: To reduce the sintering temperature in the microstructural design of $\alpha\text{-Al}_2\text{O}_3$ -based ceramics, a mixture of basalt glass and yttria-stabilized zirconia (YSZ) was used. The effect of isothermal holding time during liquid-phase sintering of a composite containing 85 wt.% $\alpha\text{-Al}_2\text{O}_3$ and 15 wt.% (basalt glass + YSZ) on its mechanical properties was investigated. The samples were sintered at temperatures of 1450 and 1500 °C for 2–6 hours. It was established that sintering occurs in the presence of a liquid phase that persists throughout the entire holding period, and the densification of the material is determined by the rearrangement and Ostwald ripening processes of Al_2O_3 grains. The maximum hardness reached 7.73 GPa, while the fracture toughness reached 7.95 $\text{MPa}\cdot\text{m}^{1/2}$. The effect of microstructural evolution on the hardness and fracture toughness of the composite was demonstrated.

KEYWORDS: ALUMINA, BASALT GLASS, ZIRCONIA, LIQUID PHASE SINTERING, HARDNESS, FRACTURE TOUGHNESS.

1. Introduction

Al_2O_3 is characterized by one of the best cost-to-properties ratios among modern ceramic materials [1]. The widespread application of ceramic materials based on $\alpha\text{-Al}_2\text{O}_3$ in various industrial sectors is attributed to the combination of their chemical, mechanical, thermal, electrical, and optical properties. However, despite these advantages, the using of Al_2O_3 as a structural material is limited by its low fracture toughness [2]. Microstructural design of advanced structural materials based on $\alpha\text{-Al}_2\text{O}_3$ is aimed at reducing the sintering temperature and overcoming the brittleness problem [3], [4].

2. Prerequisites and means for solving the problem

The reduction of the sintering temperature of Al_2O_3 based ceramics below 1600–1700 °C is promoted by additives that form a liquid phase during heating. The liquid phase appears either the melting temperature of the additives is lower than the sintering temperature or new phases with melting temperatures below the sintering temperature are formed as a result of interactions between the components [4]. Various additives are used in the sintering of $\alpha\text{-Al}_2\text{O}_3$ based ceramics, among which multicomponent additives have attracted considerable attention [5] – [7]. This promotes to lowering the sintering temperature, increasing the density, and improving the mechanical properties of the ceramics.

To improve fracture toughness of Al_2O_3 -based ceramics, zirconia-toughened alumina (ZTA) have been developed. In these ceramics, particles of unstabilized ZrO_2 or a tetragonal solid solution based on ZrO_2 stabilized with Y_2O_3 are dispersed within an $\alpha\text{-Al}_2\text{O}_3$ matrix. The improvement in fracture toughness of ZTA composites is achieved through the combined action of transformation toughening caused by the stress-induced martensitic phase transformation of tetragonal ZrO_2 -based solid-solution particles into the monoclinic phase ($\text{T-ZrO}_2 \rightarrow \text{M-ZrO}_2$), together with microcracking, crack deflection, and the formation of compressive surface stresses. ZTA composites are typically sintered at 1600 °C [8] – [10].

3. Solution of the examined problem

Various types of natural rocks can be utilized in the development of materials with varied microstructures and physic mechanical properties due to their unique multicomponent mineralogical and chemical compositions [11]. Igneous basalt-like rocks, which undergo a special technological treatment involving melting, are finding increasingly widespread applications in the production of various materials and products [12]. Since rocks are products of the solidification of natural silicate melts, their melting begins with softening at 1050–1070 °C and progresses to intensive melting at approximately 1450 °C. Melts of igneous rocks differ from glass melts in that they are produced at higher temperatures and do not involve a silicate-forming stage. Unlike glasses obtained by melting a charge (a blend of raw materials in the required proportions), the components involved in the melting of rocks are not individual oxides but rather mineral compounds, including

pyroxene, augite, olivine, diopside, anorthite, and others. Furthermore, the structure characteristic of the parent rock, together with its specific mineralogical composition, is retained in the melt [13]. The use of basalt glass to reduce the sintering temperature of $\alpha\text{-Al}_2\text{O}_3$ -based ceramics is consistent with the current trend in oxide ceramic development, which is based on the principles of designing medium-entropy complex-composition oxide materials [14].

To the best of the authors' knowledge, studies on Al_2O_3 /basalt glass composites have not yet been reported in the literature.

In the present study, a blend of basalt glass (BG) and a powder of a tetragonal ZrO_2 -based solid solution stabilized with Y_2O_3 (YSZ) was used. ZrO_2 affects the physicochemical characteristics of the basalt glass melts; however, no chemical interaction between them occurs [15]. It is known that increasing the Al_2O_3 content raises the glass-transition and crystallization temperatures, increases the viscosity of rock-derived melts, and improves the mechanical properties of fibers [16]. However, data regarding the chemical interaction between Al_2O_3 and basalt glass melts are not available in the literature.

The aim of this study was to investigate the effect of the isothermal holding time during liquid-phase sintering on the mechanical properties of a composite with the composition 85 wt.% $\alpha\text{-Al}_2\text{O}_3$ –15 wt.% (BG + YSZ), where the liquid phase persists throughout the entire isothermal holding period.

Alumina powder of $\Gamma\text{-OO}$ grade and basalt glass powder were selected for the study; the latter was obtained by melting a rock of transitional composition between basic (basalts) and intermediate (andesites), followed by grinding in a ball mill. The powder of a ZrO_2 -based solid solution stabilized with 3 mol.% Y_2O_3 (YSZ) was synthesized by the hydrothermal method in an alkaline medium [17], [18].

A powder blend with the composition 85 wt.% $\alpha\text{-Al}_2\text{O}_3$ – 15 wt.% (BG + YSZ) was mixed in a ball mill in an isopropyl alcohol medium for 2 h and subsequently dried in air at 80 °C for 24 h. Green bodies were formed by cold uniaxial double-sided pressing in a steel die under a pressure of 50 MPa. A 5 wt.% aqueous solution of polyvinyl alcohol in distilled water was used as a binder during powder preparation.

The formed specimens (three samples for each sintering holding time) were dried in air at 80 °C for 24 h. The green compacts, with a diameter of 20 mm and a height of 6 mm, exhibited a relative density of 0.40. The samples were sintered in a Nabertherm LTH08/17 laboratory electric furnace at 1450 °C and 1500 °C for 2, 4, and 6 h, followed by cooling in furnace. Fracture surfaces and polished longitudinal cross-sections of the sintered specimens had been prepared for investigations.

The properties of the samples were investigated by X-ray diffraction (XRD) using a DRON-1.5 diffractometer equipped with a digital data acquisition system ($\text{CuK}\alpha$ radiation, scanning rate 1–4° min^{-1} , $2\theta = 15\text{--}90^\circ$) and by scanning electron microscopy (SEM) using an Axia ChemiSEM microscope (Thermo Fisher Scientific, USA). Mechanical properties were evaluated using a Falkon 509 hardness tester (Netherlands) with an indentation load of 300 N (30 kgf). The fracture toughness factor (K_{IC}) of the composites was calculated according to [19].

4. Results and discussion

The specific surface area of the initial powder mixture with the composition (wt.%) 85 α -Al₂O₃ – 15 (BG + YSZ) was 53.14 m²/g. The mixture contained (wt.%): 84.852 Al₂O₃, 6.763 SiO₂, 1.907 Fe₂O₃, 0.527 MgO, 3.190 ZrO₂, 0.262 Y₂O₃, 0.290 Gd₂O₃, 0.413 K₂O, and 0.215 TiO₂. The theoretical density, calculated using the rule of mixtures, was 3.67×10^3 kg/m³. According to the X-ray diffraction (XRD) analysis, reflections characteristic of α -Al₂O₃ and a low-angle amorphous halo associated with the presence of basalt glass in the mixture were identified.

It is well known that liquid-phase sintering is conventionally divided into three stages according to the dominant densification mechanisms: (1) viscous flow of the liquid phase accompanied by rearrangement of solid particles; (2) dissolution–precipitation, or recrystallization through the liquid phase; and (3) formation of a rigid skeleton followed by sintering controlled by solid-state diffusion mechanisms [20]. The temperatures of 1450 °C and 1500 °C correspond to the melting range of basalt glass. Regardless of the holding time, sintering of the composite with the composition 85 wt.% α -Al₂O₃ – 15 wt.% (BG + YSZ) were proceeded in the presence of a liquid phase that persists throughout the entire isothermal holding period. Therefore, the solid-state sintering stage was absent under the present experimental conditions.

The relative density of the sintered samples was determined by hydrostatic weighing (Archimedes method). After sintering at 1450 °C, the relative density increased to 0.89, whereas after sintering at 1500 °C it reached 0.96. The volumetric shrinkage of the specimens was 57–58%. Such high shrinkage is a characteristic feature of liquid-phase sintering and depends, to a certain extent, on the wettability of the solid phase by the liquid. During volumetric densification, the principal driving forces are capillary forces generated by the liquid phase [20].

It can be assumed that the decisive factor in the high shrinkage of the samples during sintering is the nanocrystallinity of the initial α -Al₂O₃ powder and the wettability of Al₂O₃ by the basalt glass melt. The main mechanisms responsible for shrinkage during liquid-phase sintering of the composite are particle rearrangement and Ostwald ripening of α -Al₂O₃ grains [21].

After 2 h of sintering at both temperatures, Al₂O₃ grains of rounded and platelet-like morphology with various sizes were observed in the samples (Fig. 1a, d). While nanosized rounded Al₂O₃ grains remained after sintering at 1450 °C, their size increased to 1–2 μ m after sintering at 1500 °C. The lateral dimension of the platelet-like grains varied from 2–5 μ m up to 10 μ m. It is evident that their size was considerably larger after sintering at 1500 °C. The diameter of rounded pores ranged from 1–2 μ m to 5–7 μ m. Elongated pores reached lengths of up to 10 μ m after sintering at 1450 °C, whereas their length decreased by approximately two times after sintering at 1500 °C (Fig. 1a, d).

When the holding time is increased to 4 hours during sintering, the basalt glass melt fills the large pores and pore channels, leaving exclusively isolated pores. After sintering at 1450 °C, the Al₂O₃ grain size was approximately 2–3 μ m. At 1500 °C, the size of Al₂O₃ grains of various morphologies increased by a factor of 1.5–2 (Fig. 1b, e).

The grains size of Al₂O₃ practically does not increase after sintering at 1450 C for 6 hours (Fig. 1,c). After sintering at 1500 C, rounded Al₂O₃ grains up to 5 μ m in diameter and plate-like grains measuring up to up to 5–7 μ m remained. The number of Al₂O₃ grains in the form of plates up to 10 μ m in length increased (Fig. 1,f). Isolated rounded pores were preserved in the samples.

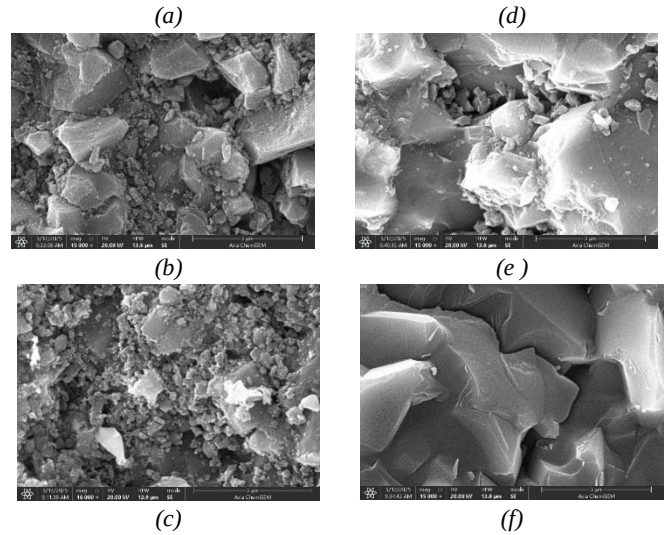
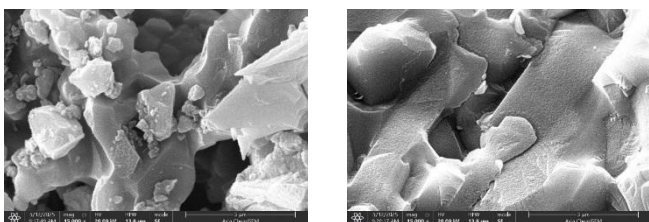


Fig. 1. SEM images of fracture surfaces of samples sintered for 2 h (a), 4 h (b), and 6 h (c) at 1450 °C, and for 2 h (d), 4 h (e), and 6 h (f) at 1500 °C

At both sintering temperatures, increasing the holding time resulted in the formation of agglomerates of irregularly shaped YSZ grains. This is a characteristic feature of ZrO₂ behavior in basalt glass melts [18]. It may therefore be assumed that, in the present case, the evolution of microstructural constituents has a greater influence on the mechanical properties of the composite with the composition 85 wt.% α -Al₂O₃ – 15 wt.% (BG + YSZ) than the presence of ZrO₂ itself.

Self-organization of the composite with the composition 85 wt.% α -Al₂O₃ – 15 wt.% (BG + YSZ) during sintering at 1450 °C leads to the formation of a two-scale structure. Within a matrix of smaller α -Al₂O₃ grain conglomerates, "densified" zones are formed, containing platelet-shaped α -Al₂O₃ grains up to 3 μ m in length within the solidified basalt glass (Fig. 2).

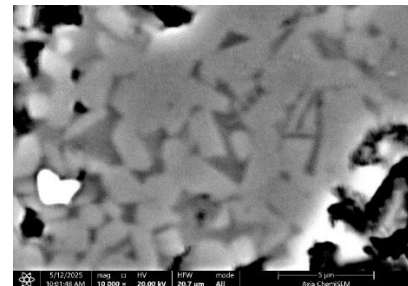


Fig. 2. Microstructure of the "densified" zones formed during sintering at 1450 °C. The bright phase corresponds to YSZ particles

The microstructural evolution during sintering at 1500 °C differs in that no "densified" zones are formed after 2 and 4 h of sintering. Under these conditions, isolated rounded and elongated pores are observed, with sizes decreasing to 1–2 μ m and approximately 10 μ m, respectively. Increasing the holding time to 6 h results in the formation of a two-scale microstructure within the composite. Isolated regions are formed in which platelet-like and polygonal Al₂O₃ grains are embedded in the solidified basalt glass melt.

At 1450 °C, the hardness of the ceramic continuously increases from 6.56 GPa to 7.56 GPa as the holding time is extended from 2 to 6 h (Fig. 3a). At 1500 °C, the hardness increases from 6.65 GPa to 7.71 GPa when the holding time is increased from 2 to 4 h and remains essentially unchanged (7.73 GPa) after 6 h of sintering (Fig. 3a).

The fracture toughness (K_{IC}) of the ceramic increases from 5.55 MPa·m^{1/2} to 5.95 MPa·m^{1/2} after sintering at 1450 °C. In contrast, after sintering at 1500 °C, the fracture toughness decreases from

7.95 MPa·m^{1/2} to 6.14 MPa·m^{1/2} when the holding time is increased from 4 to 6 h (Fig. 3b).

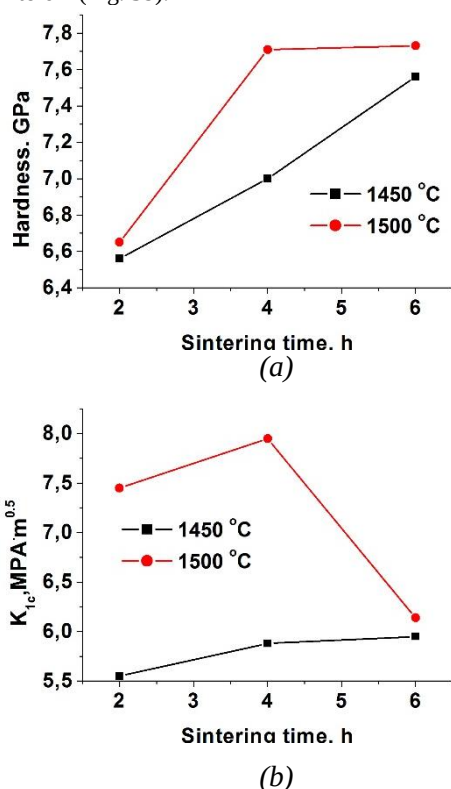


Fig. 3. Dependence of hardness (a) and fracture toughness, K_{IC} (b), of the sintered samples on the sintering holding time

The evolution of the composite microstructure results in an increase in hardness to 7.56 GPa and fracture toughness (K_{IC}) to 5.95 MPa·m^{1/2} in the presence of densified regions formed during sintering at 1450 °C. The absence of these regions and the higher density achieved after sintering at 1500 °C lead to increases in hardness and fracture toughness (K_{IC}) to 7.71 GPa and 7.95 MPa·m^{1/2}, respectively. However, the subsequent formation of densified regions during prolonged sintering at 1500 °C reduces the mechanical properties of the ceramic to values comparable to those obtained after sintering at 1450 °C.

5. Conclusions

Microstructural designing of ceramic composites is based on understanding the mechanisms of formation of the structure elements under various thermodynamic conditions, as well as the nature of their influence on the properties of ceramics.

Sintering of the composite with a composition of 85 wt.% α -Al₂O₃ – 15 wt.% (BG + YSZ) at 1450–1500 °C occurs in the presence of a liquid phase that persists throughout the entire isothermal holding period. The sintering behavior of the composite is predominantly determined by the rearrangement and Ostwald ripening of Al₂O₃ grains.

The features of structure formation during sintering are determined by the synergistic effect of α -Al₂O₃, YSZ, and basalt glass, due to the absence of interaction between them, as well as the evolution of the structural components. A characteristic feature is the formation of a two-scale microstructure. "Densified" zones are formed in the samples, containing α -Al₂O₃ platelets in the solidified basalt glass.

Upon the formation of a two-scale microstructure after sintering the composite at 1450 °C, its hardness increases to 7.56 GPa and the fracture toughness (K_{IC}) reaches 5.95 MPa·m^{1/2}. Raising the sintering temperature to 1500 °C and extending the holding time from 2 to 6 hours leads to an increase in the composite's hardness from 6.65 GPa to 7.73 GPa. The formation of the two-scale microstructure contributes to a decrease in fracture toughness from 7.95 MPa·m^{1/2} to 6.14 MPa·m^{1/2} as the holding time is increased from 4 to 6 hours.

6. References

1. P. M. Kamakhya, R.D.K. Misra, Else Ser. Adv. Ceram. Mater. 21-43 (2022)
2. L. I. Osayande, I. O. Okenwa, Int. J. Appl. Ceram. Technol. **5**(3), 313-323 (2008)
3. Z. Yu, Y. Zheng, J. Sun, J. Zhao, Int. J. Refract. Met. Hard Mater. **134**, 107436 (2026)
4. M. M. R. A. Lima, R. D. C. C. Monteiro, Ceram.: Process. Reliab. Tribol. Wear. **12**, 178-183 (2000).
5. Z. Yajun, L. Kefeng, G. Haoyu, S. W. H. Xiangyu, S. Guodong, D. Zhiming, S. Yu, Ceram. Int. **51**, 54515–54529 (2025)
6. O. R. K. Montedo, P. C. Milak, C. A. Faller, M. Peterson, E. Angioletto, J. Therm. Anal. Calorim. **124**(1), 241-249 (2016)
7. R. Yang, Y. Yang, Y. Wang, Q. Chang, J. Zhou, Sep. Purif. Technol. **323**, 124231 (2023)
8. I. Žmak, D. Čorić, V. Mandić, L. Čurković, Mat. **13**, 122 (2020)
9. M.Yu. Smyrnova-Zamkova, O. K. Ruban, O. I. Bykov, M. Ya. Holovchuk, T. V. Mosina, O. I. Khomenko, E. V. Dudnik, Powder Metall. Met. Ceram. **60**/3 129–141 (2021)
10. O. Fakolujo, A. Merati, M. Bielawski, M. Bolduc, M. Nganbe, J. Miner. Mater. Charact. Eng., **4**, 87-102 (2016)
11. L. Felippi de Lima, J. E. Zorzi, R. C. D. Cruz, Bol. Soc. Esp. Ceram. Vidr. **61**, 2–12 (2022)
12. I. I. Diduk, Yu. M. Chuvashov, O. M. Yashchenko, N. I. Koshelenko, Budiv. Mater. Vyr. **3**–4 54–56 (2018)
13. D. D. Dzhigiris, M. F. Makhova, Osnovy proizvodstva bazaltovykh volokon i izdeliy, Moscow: Teploenergetik., 412 (2002)
14. A. J. Wright, J. Luo, Jour. Mater. Resear. **55**, 9812-9827 (2020)
15. I. Diduk, G. A. Bagliuk, Mach. Tech., Mat. **2**, 15-18 (2016)
16. D. Xing, X. Xi, M. Peng-Cheng, Appl. Sci. Manuf. Compos. A **119**, 127-133 (2019)
17. E. V. Dudnik, A. V. Shevchenko, Powder Metall. Met. Ceram. **49**/3–4, 125-134 (2010)
18. I. O. Marek, O. K. Ryban, V. P. Red'ko, M. I. Danylenko, S. A. Korniy, O. V. Dudnik, Powder Metall. Met. Ceram. **58**/3–4, 125-132 (2019)
19. B. A. Galanov, O. N. Grigoriev, Elektronnyaya mikroskopiya i prochnost' materialov, **14**, 4-42 (2006)
20. M. G. Randall, S. Pavan, J. Seong, J. Mater. Sci. **44**, 1-39 (2009)
21. M. A. Behrens, A. Franzén, S. Carlert, U. Skantze, L. Lindfors, U. Olsson, Soft Matter. **21**, 2349-2354 (2025).

Tolerance treatment of sliding pairs and repeatability in assembly

Štefan Václav^{1,*}, Jozef Peterka¹
Slovak University of Technology, Slovakia¹
stefan.vaclav@stuba.sk

Abstract: The basic prerequisite for trouble-free assembly of moving structures is that the assembled structure has as many degrees of freedom as its function requires. In practice, we often encounter cases of statically overdetermined pairs. Designers often use them to increase the rigidity of products. This article describes a way to mitigate the consequences of problematic assembly in sliding pairs, which are often statically overdetermined. The article also addresses an important problem in assembly, which is repeated assembly accuracy, especially when designing assembly lines and automated and robotic systems.

Keywords: ASSEMBLY, KINEMATIC PAIRS, TOLERATION, REPEATED PRECISION

1. Introduction

In practice, the cases of statically redetermined couples are often encountered. The designers like using them to enhance rigidity of the product. A typical example is a ball bearing, which should theoretically have the maximum of three balls, but it has more of them in order to increase their toughness.

2. Statics in assembly

Figure 1 illustrates a hydraulic press that is statically redetermined. When the support moves on two cylinders, the couple is clearly statically redetermined, as shown in the Grübler - Valentovič equation [1, 2], according to which the number of degrees of freedom is minus two.

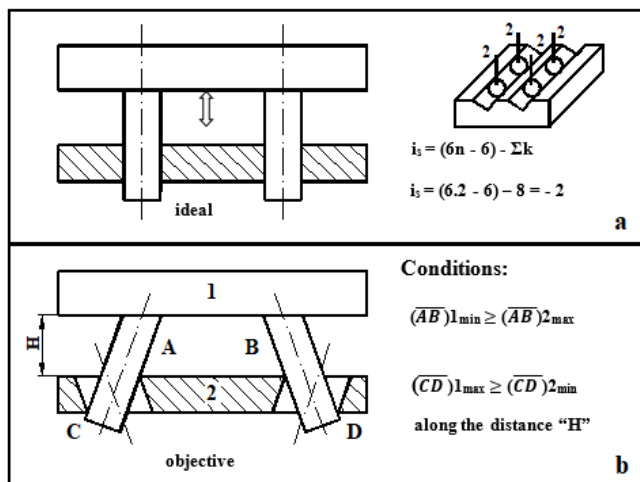


Fig.1: Toleration treatment of statically redetermined movable couples

There are more conditions for trouble-free assembly regarding the fact that the couples are not parallel but concurrent or even skewed. In such circumstances, the couple must have gaps enabling smooth assembly even despite non-parallelism of the couple, which in turn partially decreases toughness.

It is often necessary to bond two elements (Figure 1) which apparently form a statically redetermined kinematic couple.

This concerns also a flanged bond, e.g. the bond of white and black flanges with four pins (Figure 2a). It is desirable to label both parts in order to enable assembly in any case (trouble-free assembly).

Figure 3 shows a different method of mitigating the consequences of troublesome assembly of very frequent sliding couples which are generally statically redetermined. The couple depicted in Figure 3a is evidently statically redetermined; the consequences may be mitigated when first assembling the sliding workbench with rods and then connecting them to the base (Figure 3b).

Figure 3c is the best illustration of trouble-free assembly: there are two rotary-sliding couples (four-point) on one shaft, and a one-point couple on the other one (touches the left or the right side). Such a structure is statically redetermined but definite, which may assure completely trouble-free assembly.

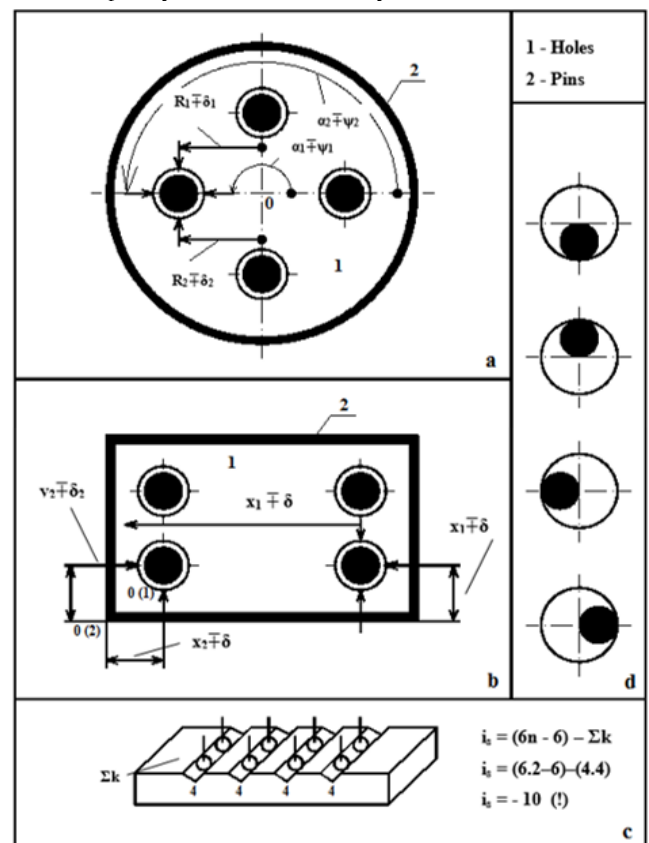


Fig.2: Assemblability of statically redetermined unmovable couples. a, b – dimension method, c – number of degrees of freedom, d – assemblability check

Figure 3 shows a different method of mitigating the consequences of troublesome assembly of very frequent sliding couples which are generally statically redetermined. The couple depicted in Figure 3a is evidently statically redetermined; the consequences may be mitigated when first assembling the sliding workbench with rods and then connecting them to the base (Figure 3b).

Figure 3c is the best illustration of trouble-free assembly: there are two rotary-sliding couples (four-point) on one shaft, and a one-point couple on the other one (touches the left or the right side). Such a structure is statically redetermined but definite, which may assure completely trouble-free assembly.

If high accuracy in the product is not needed, so called extenders of gaps can be used. The principle is shown in Figure 4.

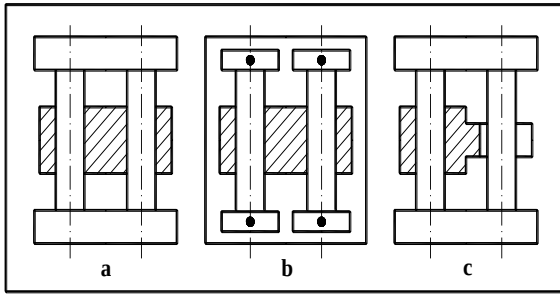


Fig.3: Assemblability of movable couples [3]. a – statically redetermined structure, b – gradual assembly of statically redetermined structure, c – statically determined structure (trouble-free assembly).

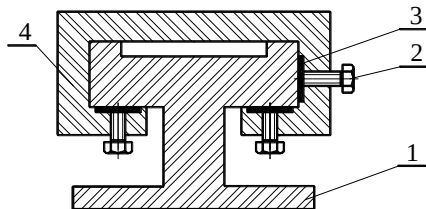


Fig.4 Assemblability of movable couples. Demands for precision will decrease when using extenders of gaps. 1 – frame, 2 – screws, 3 – extenders, 4 – bench.

3. Statics repeated precision of assembly

A very important issue in assembly is repeated accuracy, especially when constructing assembly lines (Figure 5).

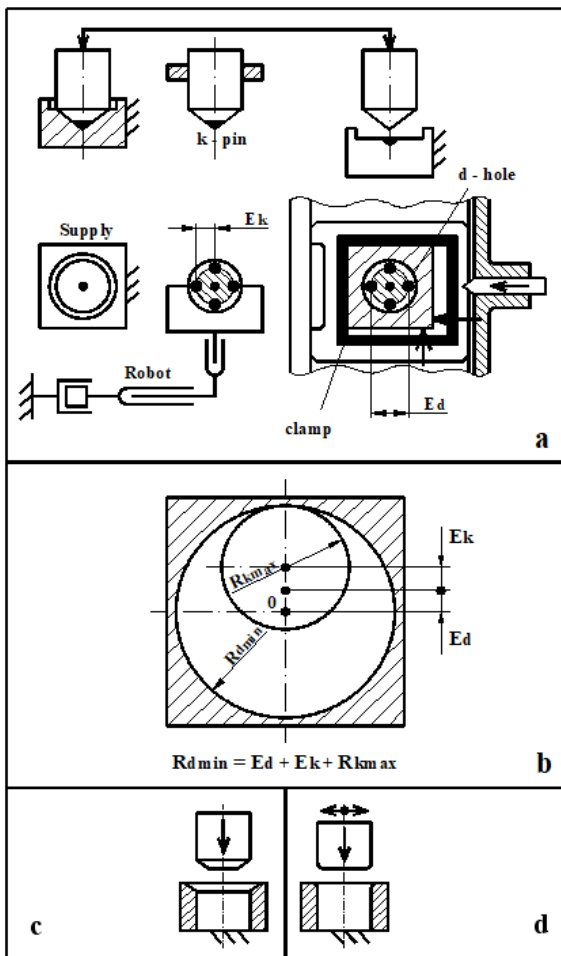


Fig.5 Repeated accuracy of the robot and clamp increases the probability of the insertion of pin into hole [4]. a – robot and clamp, b – conditions of insertion, c – chamfers improve probability of insertion, d – vibration improves probability of insertion.

Inaccuracy of the robot inserting the pin into the hole may cause the inaccuracy of the hole location in the gripper, which may prevent a successful insertion of the pin into the hole (Figure 5a).

This may be due to the reasons described below [4]. The first reason for the failure of assembly is that a robot collecting pins from the palette has a certain repetitive accuracy (uncertainty) of positioning, i.e. when inserting the pins, their spikes are not positioned to the same point (position), but make a circle of eccentricity “ E_k ” (Figure 5a).

Another reason for the failure of assembly is that the center of the hole is not in the same place with respect to the frame of the machine, but may be in a different place in each clamp, which is due to inaccuracy of the gripper and clamp, and sometimes also due to inaccurate contours of the part in the clamp (Figure 5a).

The issue poses a problem since the two causes may be combined (inaccuracies may increase by mutual summation) and it can be easily proved (Figure 5b) that to insert a pin by the radius R_{kmax} into the hole, the radius of the hole must be:

$$R_{dmin} = E_d + E_k + R_{kmax} \text{ [mm]} \quad (1)$$

where:

R_{dmin} – minimum radius of opening [mm],

E_d – eccentricity of opening [mm],

E_k – eccentricity of pin [mm],

R_{kmax} – maximum radius of pin [mm].

From experience it is known that such assembly requires a disproportionately large gap between the pin and the hole. This can be eliminated by using the maximum chamfer of both components (Figure 5c) and then trying to insert the pin into the hole by utilising flexibility.

Another option is a little more complicated: the pin is placed next to the hole and then oscillatory motions are performed until success is achieved, under some pressure, to capture the pin into the hole (Figure 5d).

4. Conclusion

Online references will be linked to their original source, only if possible. To enable this linking extra care should be taken when preparing reference lists.

The above-mentioned suggests that the shorter and of better quality the line, the lower the values of E_k and E_d . As illustrated in Figure 5b, assembly will be trouble-free under the following condition:

$$R_{dmin} = E_d + E_k + R_{kmax} \text{ [mm]} \quad (2)$$

or for the diameters:

$$(\varnothing_{dmin})/2 = E_d + E_k + (\varnothing_{kmax})/2$$

$$\varnothing_{dmin} = 2E_d + 2E_k + \varnothing_{kmax} \text{ [mm]} \quad (3)$$

After supplying particular values, e.g. $\varnothing_{kmax} = 40.1 \text{ mm}$, $E_k = 0.2 \text{ mm}$, $E_d = 0.1 \text{ mm}$:

$$\varnothing_{dmin} = 0.2 + 0.4 + 40.1 = 40.7 \text{ [mm]}$$

Such a large gap (0.7 mm) cannot be accepted; the diameter of the hole will be therefore reduced. From experience it is known that the gaps between pin and hole will be disproportionately large in such assembly.

The gap can be eliminated by using the maximum chamfer of both parts (Figure 5c) and then applying flexibility to insert the pin into the hole.

Another option is a little more complicated: the pin is placed next to the hole and then oscillatory motions are performed until

success is achieved, under some pressure, to capture the pin into the hole (Figure 5d).

The machine to carry out such operations must be fitted with artificial sight and feeling. Such systems are very complex.

5. Acknowledgements

The article was supported by the VEGA 1/0391/24 project "Research and development of a methodology for calibrating diagnostic equipment sensors for automated and robotic systems" supported by the scientific grant agency of the Ministry of Education of the Slovak Republic and of Slovak Academy of Sciences.

6. References

1. E. Valentovič, Geometric and static conditions of assembly. In: Assembly Automation, **No 3**, pp. 233-236, (2000)
2. E. Valentovič, Knowing your orientation. In: Assembly Automation, **No. 2**, pp.31-33, (1996)
3. Š. Václav, *Objective method for assembly*. - 1st Edition. - Köthen: Hochschule Anhalt, - 102 p. - ISBN 978-3-86011-044-7, (2011)
4. Š. Václav, *Vybrané state z teórie montáže. (Selected chapters form the theory of assembly)* Habilitation thesis. - Trnava: STU v Bratislave MTF UVTE. 104 p. (2012)

Influence of thermodynamic properties of metallic materials on the efficiency of hydro-vacuum atomization and hydriding processes

David Sakhvadze¹, Gigo Jandieri^{*1}, Besik Saralidze²,
Georgi Sakhvadze³, Anzor Kupharadze⁴, Nata Sulakvelidze⁵, Zivzivadze Onise⁶

Rafiel Dvali Institute of Machine Mechanics ¹ – Tbilisi, Georgia; Ferdinand Tavadze Institute of Material science and Metallurgy ³ – Tbilisi, Georgia; Metal Powder Ltd ⁴ – Tbilisi, Georgia; Novel Visio & G3D Ltd⁵ – Georgia; Akaki Tsereteli State University ⁶ – Kutaisi, Georgia
*e-mail: gigo.jandieri@gmail.com

Abstract: *In this study, we present the key results of computer modeling and experimental series of a combined technological process that integrates hydro-vacuum atomization and hydrogenation of metallic melts. The simulations considered several representative cases in which lead, aluminum, magnesium, Armco iron, and magnesium–aluminum alloys were used as initial materials. A comparative analysis of the obtained data revealed that, during hydro-vacuum atomization, the cooling, solidification, and hydrogenation kinetics of atomized droplets are strongly governed by the specific thermodynamic characteristics of the metals, such as the solidification interval, latent heat of fusion/solidification, and specific heat capacity. It was established that the relationship between the melt overheating temperature and the width of its solidification interval constitutes a key controlling factor in the combined processes of atomization and hydrogenation. This factor is critical because it determines both the duration and the nature of the residence of atomized metallic droplets in the transitional liquid–crystalline state, thereby defining the temporal window and the depth of highly effective physico-technological influences that promote hydrogen uptake. These influences arise during the entrainment and breakup of the melt jet in the water stream and include hydromechanical activation, structural metastabilization, and interstitial hydrogen incorporation released from collapsing cavitation cavities in water due to the thermobaric energy generated during their directed cumulative implosion.*

KEYWORDS: HYDRO-VACUUM ATOMIZATION, CRYSTALLIZATION KINETICS, HYDROGENATION, STRUCTURAL METASTABILIZATION, OVERHEATING EFFECT.

1. Introduction

The use of metallic powders as solid-state hydrogen carriers opens new prospects for the development of safe, energy-efficient, and compact systems for the storage and transportation of renewable energy.

In contrast to conventional methods of hydrogen storage in gaseous or cryogenically liquefied form, metallic powder materials enable hydrogen retention in a chemically bound state (as metal hydrides formed through chemisorption mechanisms) or physically, through adsorption on the developed surface of the particles. This approach provides a substantially higher level of operational safety and allows long- term hydrogen storage under ambient conditions without the need to maintain extremely high pressures or ultralow temperatures. Moreover, the use of powder-based metal hydride materials completely eliminates the risks and operational costs associated with high- pressure composite vessels (600–700 bar) or cryogenic cooling systems operating at 20–70 K, both of which require complex infrastructure and expensive reinforced containment shells [1]. Unlike conventional hydrogen storage technologies, the retention of hydrogen in a chemically bound metal- hydride state, followed by its controlled thermal release upon heating the metal to approximately 100–300 °C, is characterized by a high degree of controllability and operational reliability. The desorption process proceeds smoothly, and its kinetics can be effectively regulated by adjusting the temperature of the hydrogenated material. This enables precise modulation of the hydrogen release rate in accordance with the specific demands of the system [2].

An equally important operational criterion is the high reversibility and stability of the hydrogenation–dehydrogenation cycles. The ability of a material to withstand numerous working cycles without significant structural degradation or loss of reversible hydrogen capacity determines the long- term durability of powder- based metal hydride storage systems and their technological applicability in the practical energy sector.

High- cycle metal hydride systems are particularly in demand in hydrogen- powered transportation, from unmanned aerial vehicles to heavy commercial machinery, as well as in autonomous and backup energy complexes for remote facilities, in decentralized

storage systems for renewable energy, and in stationary hydrogen reservoirs used in “green” metallurgy and the chemical industry [3, 4].

The successful integration of metal hydride systems into the aforementioned high- technology sectors is largely determined by the morphological and thermodynamic characteristics of the hydrogen- storage materials. A highly developed specific surface area in powder- based materials provides a dense population of active sorption sites, significantly accelerating the kinetics of diffusive or chemisorptive hydrogen uptake and saturation. However, morphological optimization alone is insufficient to overcome the fundamental limitations that hinder large- scale commercial deployment of such storage media. The primary barrier remains the stringent thermodynamic constraints associated with the high thermal stability of certain hydride phases, which result in sluggish desorption kinetics and necessitate elevated temperatures for reversible hydrogen release [5]. Moreover, these kinetic limitations become progressively aggravated over time due to the advancing structural degradation of the material. During high- temperature operation, cyclic phase hardening induces fragmentation (cracking) of the particles, followed by thermocyclic sintering and passivation [6, 7]. These processes lead to an irreversible reduction in sorption capacity and effectively negate the initial advantages associated with a highly developed specific surface area. Consequently, this indicates that the operational efficiency of reversible metal hydride systems is governed by a fundamental compromise between the thermodynamic stability of the hydride phases formed and the kinetic parameters of the sorption–desorption processes. For example, on the one hand, hydrides of light metals and their complex compounds (MgH₂, LiBH₄, Mg(BH₄)₂, AlH₃, TiH₂) exhibit exceptionally high theoretical hydrogen capacities, ranging from 4 to 18.5 wt.% H₂. However, such high storage capacities are achieved at the expense of thermodynamically robust metal–hydrogen bonds, which require substantial energy input for subsequent dissociation and shift the desorption temperature range into the domain of elevated temperatures (>250–500 °C). This is undesirable both from the standpoint of process efficiency and due to the reduction in the operational lifetime of the storage system. On the other hand, intermetallic compounds, such as Laves phases based on AB₂- and

AB₅- type alloys (LaNi₅, TiFe, ZrMn₂), enable operation under moderate, near- ambient thermal conditions ($\approx 50\text{--}100\text{ }^{\circ}\text{C}$) [8, 9]. Nevertheless, their hydrogen storage capacity is significantly lower than that of light- metal hydrides and typically does not exceed 1.4–2 wt.% H₂. This limitation restricts their applicability in technical systems where high specific energy density is a critically important requirement.

A compromise-oriented attempt to resolve the thermodynamic–kinetic contradiction involves transitioning to lighter binary systems, among which intermetallic alloys of the Mg–Al system are of particular interest. The Mg₁₇Al₁₂ and Mg₂Al₃ phases occupy an intermediate position between high- capacity yet thermodynamically stable light- metal hydrides and low- temperature but low- capacity intermetallic compounds. The incorporation of aluminum into the magnesium matrix partially reduces its thermodynamic stability while maintaining a relatively high specific hydrogen capacity. For the Mg₁₇Al₁₂ phase, the theoretical hydrogen storage capacity is approximately 4.0–4.4 wt.% H₂, and due to the destabilizing influence of aluminum, the desorption enthalpy decreases to 65–70 kJ/mol H₂ (compared to ~ 75 kJ/mol for the pure Mg–H system). This results in a shift of the hydrogen release temperature threshold into the range of 150–280 $^{\circ}\text{C}$ and a noticeable improvement in desorption kinetics [10, 11].

Nevertheless, even the use of such metastabilized alloys does not fully eliminate the fundamental thermodynamic–kinetic dualism and ultimately imposes strict limitations on the choice of metallic materials and the methods by which they can be hydrogenated.

2. Modern approaches to solving the existing problem and substantiating the effectiveness of the hydro-vacuum method

Based on current scientific knowledge and accumulated practical experience, a wide range of methods has been developed to address the aforementioned problem. For example, modern catalytic approaches [12] demonstrate high efficiency in improving hydrogenation kinetics; however, the use of noble metals (Pt, Pd) is limited by their high cost and susceptibility to deactivation due to oxidation and impurity poisoning, which reduces the cyclic durability of such metal-based systems.

Mechanical alloying [13] provides high dispersion ($< 50\text{ }\mu\text{m}$) and stable formation of defect-rich states, but requires prolonged processing and is accompanied by powder contamination from wear products of the milling media.

Plasma- arc synthesis [14], in turn, is applicable only to a narrow class of hydride systems, primarily to compounds such as Alane (AlH₃), and is characterized by extreme thermal gradients that complicate control over the phase composition. Other high- energy hydride- forming techniques, such as electro- pulse treatment of solid- phase suspensions in liquid dielectrics or acoustic- cavitation sonoprocessing [15–17], face challenges associated with low process stability and high energy consumption per unit of product, which significantly limits their productivity and scalability.

The combination of the aforementioned limitations and the need to resolve the existing thermodynamic–kinetic contradiction has led to a clear demand for a new- generation technology capable of integrating the stage of metallic powder structure formation with the operation of its hydrogenation. Such a technology is the innovative hydrovacuum atomization (HVA) process developed by the authors of this study [18–20].

The combined atomization–hydrogenation process implemented in the HVA method is based on a recently identified hydrophysical mechanism of condensational sonomorphosis, which is induced and sustained by the thermobaric shock- wave effects of cavitation fluctuations [21]. This process is accompanied by the in-situ incorporation of hydrogen atoms released from molecules within a supercavitating, cumulatively collapsing, and sonopulsating vapor–water mixture stream, into both the crystalline lattices of the atomized metal and energetically favorable activated

intercrystalline regions containing free electrons, resulting in the formation of interstitial covalent bonds, see Fig. 1.

Against the background of existing technological approaches for producing hydrogenated metallic powders, it can be emphasized that the synergistic combination of atomization and hydrogenation offered by the HVA technology represents a unique engineering solution that integrates the advantages of mechanochemical activation and ultrasonic (sonochemical) treatment while mitigating their key drawbacks. The principal synergistic benefit of this method lies in the coupling of deep powder dispersion with in situ hydrogen saturation within a locally vacuumized and non- stationarily cavitating hydrodynamic medium, wherein the energy released during cavitation bubble collapse and the accompanying cumulative microjets not only contribute to material fragmentation or hydrogen liberation from collapsing cavitation cavities, but also induce a directed sonomorphosis of metastable substructures. These substructures are specifically adapted for prolonged reversible cycling, mutually reversible absorption and release of atomic hydrogen, without significant deterioration of the initial hydrogen accommodation capacity.

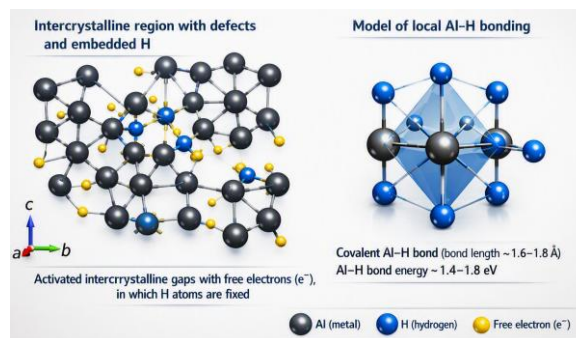


Fig. 1. Physical model of intercrystalline region and local Al–H bonding

The high density of generated crystal structure defects and the continuous exposure of pristine juvenile surfaces free from passivating oxide films ensure unobstructed diffusion and capture of hydrogen deep within the nonequilibrium metallic matrix, which acts as a structure containing numerous hydrogen traps. It should also be noted that an accompanying hydrodynamic Leidenfrost effect [22], arising at the “hot particle–liquid” interface, plays an important role in stabilizing such energetically activated structural states. The quasi- stable vapor envelope temporarily reduces the heat- transfer rate; however, its subsequent explosive collapse generates extreme quenching velocities and continuing intense acoustic- cavitation micro- impacts. These processes inhibit defect relaxation and rigidly fix the metastable, Kirkendall- effect- induced submicron- foamed structure of the powder particles formed during processing (Fig. 2).

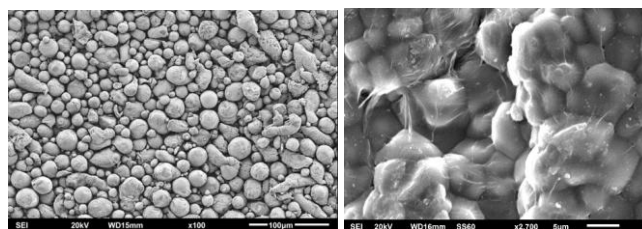


Fig. 2. SEM images of aluminum powder and surface morphology of its particles obtained by hydrovacuum atomization and hydrogenation (Bulk density not exceeding 0.5 g/cm³)

Undoubtedly, a deep understanding of the physical nature of the formation of the described structures and their subsequent controlled engineering, first requires an analysis of the fundamental thermophysical parameters of the hydrovacuum atomization process, with identification of those most critical in terms of their influence on structure formation. This emphasizes the importance

not only of selecting appropriate technological regimes for the target hydrovacuum dispersion process, but also of establishing rational conditions for the preliminary thermophysical preparation prior to feeding the liquid metallic material into the rarefied core of the counter-gravity suction and atomization chamber Fig. 3, position 1.

Consequently, understanding the mutual influence of these factors on the final (operational) characteristics of the powders represents a fundamental basis for improving the conditions of their structural formation and for more effective adaptation to the saturation and solid-state binding of atomic hydrogen.

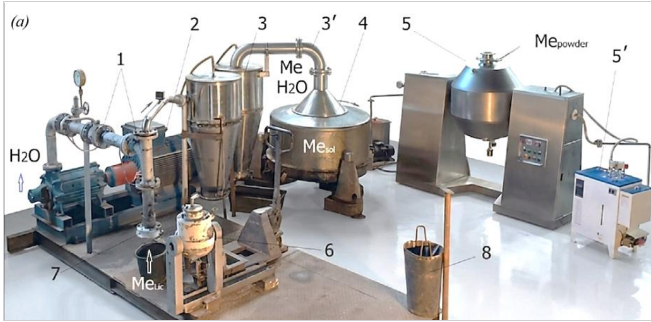


Fig. 3. General view of the hydro-vacuum atomization and hydrogenation installation for metallic melts:

- 1 — Hydro-vacuum suction, dispersion, and melt-cooling chamber (Me_{lic})
- 2 — High-pressure pump for high-velocity water injection into the chamber (water delivery pressure 12–20 bar, flow rate 20–22 L/s)
- 3 — Pair of scrubbers for primary gravitational separation of coarse powder fractions (1–2.5 mm) from the forming slurry (Me)
- 3' — Pipeline for slurry transfer from the scrubbers (3) to the dewatering centrifuge (4)
- 5 — Vacuum drying chamber for dehydrated powder
- 5' — Thermovacuum station of the drying chamber (5)
- 6 — Unit for metered feeding of the melt to the disperser-cooler (1)
- 7 — Vertical melt-suction head
- 8 — Ladle supplying the melt to the feeding unit (6)

Addressing the stated problem requires a predictive assessment of the thermophysical regimes governing the structure formation of the atomized liquid metallic material. Achieving such predictive accuracy becomes feasible through computer simulation of the cooling and quenching processes experienced by the fragmented particles formed during hydro-vacuum atomization.

The application of numerical computer modeling makes it possible, in an inverse formulation, to determine the ranges of initial (input) parameters for melt preparation that are most closely aligned with the optimal conditions required for the target hydro-vacuum treatment. In this way, modeling functions as a tool that provides a closed optimization loop: from forecasting the structural states of the atomized particles to adjusting the initial technological conditions that ensure the desired properties of the final material.

3. Factors and assumptions taken into account in the simulation

1) The interaction of a high-energy water jet (velocity 200 m/s) and the melt occurs by dispersing the latter into spherical droplets with a diameter of 10–1000 μm , the cooling of which is carried out in the presence of a gasified film formed as a result of the Leidenfrost effect; 2) Under the influence of the impact force developed during the spraying of water in the disperser, the vapor film is expected to degrade and be completely removed from the surface; 3) The temperature field in the atomized metal is distributed homogeneously $T_{liq}(t)=\text{const.}$; 4) The heat exchange process between the metal and water includes both convective and radiative (thermal radiation) components; 5) The melt solidifies at a fixed temperature $T_m=T_{lic}=T_{sol}$.

Modeling and its results: For a spherical particle with an average radius r , the volume (V), mass (m) and surface area (A) are defined as follows:

$$V = (4/3) \pi r^3, m = \rho V, A = 4\pi r^2.$$

However, considering that the metal melt is dispersed into N equal number of droplet fragments so that the total mass remains unchanged, the effective surface area increases approximately as follows: $A_{eff} = AN^{1/3}$. Then, the heat radiation intensity (q_{dot} , W) from the metal fragments with a temperature T_{liq} and a velocity v will be:

$$q_{dot} = A_{eff} [h(T_{f,v})(T_{liq} - T_w) + \varepsilon \sigma ((T_{liq} + 273.15)^4 - (T_w + 273.15)^4)] \quad (1)$$

Where, $h(T_{f,v})$ -convective heat transfer coefficient of the boundary layer, depending on the effective temperature of the cooling medium (water/steam) ($T_{film}=0.5(T_{liq}+T_w)$, $W/(m^2 \cdot K)$; T_{liq} - temperature of the metal entering the dispersion chamber, $^{\circ}\text{C}$; T_w - temperature of the dispersing and cooling water, $^{\circ}\text{C}$; ε - blackness of the metal surface (emissivity); σ - Stefan-Boltzmann constant, $5.670374419 \times 10^{-8} W/(m^2 \cdot K^4)$; v - water jet velocity, m/s.

To account for the specific heat capacity (c_v , J/kg·K) of the boundary layer, the computer script uses the following simple approximation:

$$h(T_{f,v}) = \min(h_{base} + c_v \sqrt{v}, h_{max}) \quad (2)$$

Where, h_{base} is the base heat transfer coefficient under stationary conditions, and h_{max} is the maximum allowable limit (upper limit) of the coefficient. For the case of Leidenfrost stability, we obtain the following:

$$h(T_{f,v}) = 8000 + 600 \sqrt{200} \approx 16485 \quad (3)$$

When the vapor barrier degrades (breaks), the coefficient takes on the following value:

$$h(T_{f,v}) = 25000 + 600 \sqrt{200} \approx 33485 \quad (4)$$

In addition, the calculation model for the cooling rate of the metal is based on enthalpy balance and, taking into account its specific heat capacity $c_{p,liq}$ and the condition $T_{liq} > T_{sol}$, takes the following form:

$$m c_{p,liq} dT/dt = -q_{dot} \Rightarrow dT/dt = -q_{dot} / (m c_{p,liq}) \quad (5)$$

In expanded form, the heat transfer equation is formed as the following mathematical representation:

$$dT/dt = -A_{eff} [h(T_{f,v})(T_{liq} - T_w) + \varepsilon \sigma ((T_{liq} + 273.15)^4 - (T_w + 273.15)^4)] / (m c_{p,liq}) \quad (6)$$

We assume that the actual temperature of the liquid metal T_{liq} remains unchanged until the latent heat of crystallization L_f (J/kg) is completely released from the cooling fragments. That is, the metal completely solidifies when the current latent heat supply becomes zero ($L_{(t)} = 0$):

$$T = T_{sol}, T_{liq, Initial} = m L_f, dL/dt = -q_{dot}, dT/dt = 0 \quad (7)$$

After the latent heat of crystallization is completely released $L(t) = 0$ and the prerequisite for further cooling of the solid phase $T < T_{sol}$ is created, the subsequent rate of temperature change is described by the following differential equation:

$$m c_{p,sol} dT/dt = -q_{dot}, \text{ from where: } dT/dt = -q_{dot} / (m c_{p,sol}) \quad (8)$$

Where, $c_{p,sol}$ is the specific heat capacity of the metal in the solid state. And dT/dt is calculated in a similar way to the expanded heat transfer equation (6), by replacing the heat capacity of the liquid phase in it with the solid.

4. Results and discussion

The obtained modeling results, specifically t_{sol} (cooling time to the solidus temperature T_{sol}) and $t_{100^\circ C}$ (cooling time to the boiling point of water, $100^\circ C$) — were obtained for atomized particles of lead, aluminum, magnesium, Armco- iron, and Al–Mg alloys. The simulations were performed using the initial thermophysical and thermodynamic parameters (ρ , T_{lic} , $C_{p,liq}$, $C_{p,sol}$, L_f , and T_{liq}) listed in Table 1.

The resulting cooling- kinetics contour maps, shown in Figure 4, illustrate the temperature evolution of particles of different diameters during hydrovacuum atomization. These cooling kinetics maps (isotherms) reveal distinct cooling behaviors governed by the intrinsic thermal properties of each material. In particular:

Lead (Pb) demonstrates the slowest cooling due to its high density and relatively low thermal diffusivity.

Aluminum (Al) cools significantly faster, with steep temperature gradients even for larger particle diameters.

Magnesium (Mg) exhibits the most rapid cooling, driven by its low density and high thermal conductivity.

Armco- iron (Fe) shows prolonged high- temperature retention, reflecting its high melting point and substantial latent heat of fusion.

Al–Mg alloys display intermediate cooling kinetics, with the 30%Al – 70%Mg and 70%Al – 30%Mg compositions forming distinct thermal- response profiles.

Table 1

Met.	ρ , kg/m ³	T_{lic} , °C	$C_{p,liq}$, J/kg·K	$C_{p,sol}$, J/kg·K	L_f , x10 ³ , J/kg	T_{liq} , °C
Pb	10660	327.5	160	128	23	370
Al	2375	660.3	1170	900	397	700
Mg	1570	650.0	1370	1020	370	700
Fe	6980	1538	820	450	247	1600

These cooling- time fields directly determine the structurogenesis pathways of atomized droplets. The combination of particle diameter and cooling rate defines whether the droplets undergo: full crystallization, partial solidification with retained liquid cores, formation of fine- grained or amorphous structures, development of dendritic, cellular, or equiaxed morphologies, suppression or activation of diffusion- controlled transformations, hydrogen uptake and defect stabilization during hydrovacuum processing.

Comparative analysis of the modeled thermal processes shows that, following the primary influence of particle dispersity (their diameter, d) on the cooling rate, the next most significant factors are the thermophysical properties of the material and the initial temperature of the melt supplied to the hydrovacuum disperser.

Analysis of the time required for the particles to reach the boiling point of water ($100^\circ C$) reveals several key regularities:

- Effect of particle size:

For all investigated materials, the fine fraction with a diameter of $d = 0.1$ mm ($100\ \mu m$) cools to $100^\circ C$ approximately ten times faster than larger particles with $d = 1.0$ mm ($1000\ \mu m$). This behavior is governed by the increase in specific surface area as particle size decreases.

- Armco- Fe exhibits the highest cooling rate among all materials considered. Due to its high initial temperature ($1530^\circ C$) and the intense radiative-convective heat transfer, a particle with a diameter of 0.1 mm cools to $100^\circ C$ in only 0.006 s (average cooling rate $2.38 \times 10^5\ ^\circ C/s$), whereas a particle of 1.0 mm reaches $100^\circ C$ in 0.062 s (average cooling rate $2.3 \times 10^4\ ^\circ C/s$).

- Magnesium (Mg) and aluminum (Al), despite having nearly identical initial temperatures ($720^\circ C$), exhibit different cooling characteristics. Specifically, magnesium particles cool faster (for $d = 0.1$ mm: $t \approx 0.007$ s, $v \approx 8.86 \times 10^4\ ^\circ C/s$) than aluminum particles ($t \approx 0.009$ s, $v \approx 6.89 \times 10^4\ ^\circ C/s$). This difference is attributed to the lower density and caloric properties of magnesium.

- In Al–Mg alloy systems, an increase in the magnesium content leads to an intensification of the cooling process.

- For the alloy containing 30% Al – 70% Mg, the cooling time of a 0.1 mm particle down to $100^\circ C$ is $t \approx 0.008$ s ($v \approx 7.75 \times 10^4\ ^\circ C/s$), whereas for the alloy with 30% Mg – 70% Al this time increases to $t \approx 0.010$ s ($v \approx 6.20 \times 10^4\ ^\circ C/s$).

- For lead (Pb), due to its comparatively low initial temperature ($370^\circ C$), the average cooling rate varies from $5.4 \times 10^4\ ^\circ C/s$ (for $d = 0.1$ mm, $t \approx 0.005$ s) to $5.19 \times 10^3\ ^\circ C/s$ (for $d = 1.0$ mm, $t \approx 0.052$ s).

Analysis of the obtained results shows that the solidification rate (the $Me_{liq} \rightarrow Me_{sol}$ phase transition) is primarily governed by the latent heat of crystallization, the specific heat capacity, and the initial thermal interval — i.e., the degree of superheating ($T_{liq} - T_{lic}$). For example, although the crystallization temperature of Armco iron is nearly twice that of aluminum, and although aluminum is less superheated during dispersion compared to Armco iron, its solidification duration is nevertheless longer (0.03312 s vs. 0.02736 s). This behavior is explained by the fact that the latent heat of aluminum ($397\ 000$ J/kg) is significantly higher than that of iron ($247\ 000$ J/kg), and its specific heat capacity in the solid state ($C_{p,sol}$) is approximately twice that of iron.

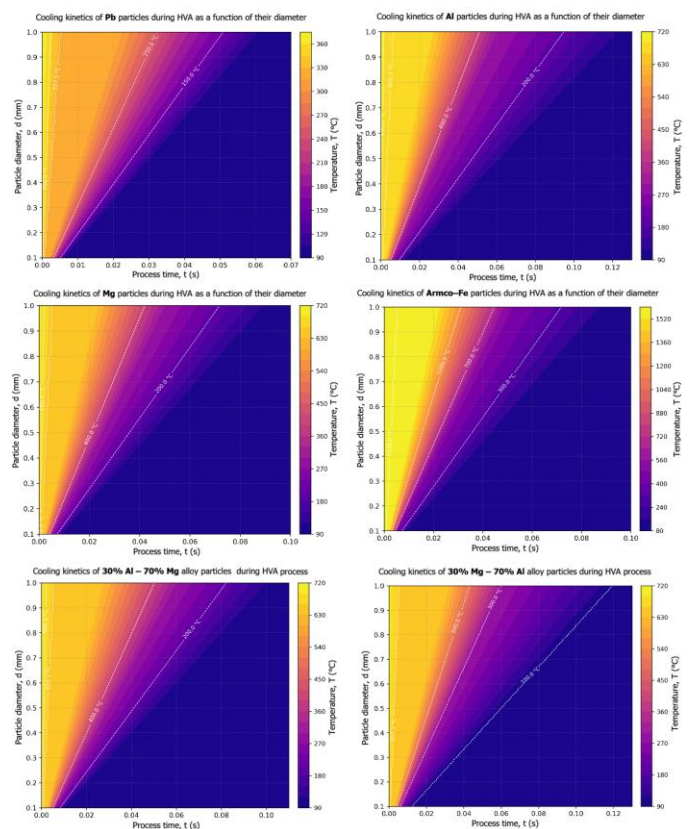


Fig. 4. Modeling results: Dependence of the cooling rate of hydrovacuum- atomized particles of lead, aluminum, magnesium, Armco-Fe, and Al–Mg alloys on dispersion duration and particle size - fraction 100–1000 μm .

In turn, analysis of the diagrams shown in Fig. 5 indicates that, due to the reduction of powder particle size to 0.01 mm ($10\ \mu m$) — and, consequently, the increase in the surface- area- to- mass ratio (A/m) — the cooling rates in this range rise sharply and reach values on the order of $10^5\ ^\circ C/s$.

In particular, analysis of the time required for particles to reach $100^\circ C$ for the extreme boundaries of the fraction ($d = 0.01$ mm ($10\ \mu m$) and $d = 0.10$ mm ($100\ \mu m$)) leads to the following findings:

For aluminum particles with a size of 0.01 mm ($10\ \mu m$), the cooling time from the initial melt temperature ($\approx 720^\circ C$) down to $100^\circ C$ is less than 0.002 s (approximately 1.8 – 2.0 ms). The

corresponding average cooling rate exceeds $6.5 \times 10^5 - 7.7 \times 10^5$ °C/s, which is characteristic of ultra- rapid solidification conditions.

For aluminum particles with a size of 0.10 mm (100 μ m), the time required to reach 100 °C is approximately 0.0125 s, and the average cooling rate is about 5.3×10^4 °C/s.

The 30% Mg – 70% Al alloy exhibits cooling dynamics similar to those of pure aluminum: a 0.10 mm particle cools to 100 °C in 0.012 s, with an average cooling rate of $\approx 5.5 \times 10^4$ °C/s.

In the 50% Al – 50% Mg alloy, due to reduced density and modified heat capacity, the cooling time of a 0.10 mm particle decreases to 0.0105 s (cooling rate $\approx 5.9 \times 10^4$ °C/s).

In turn, the 70% Mg – 30% Al alloy demonstrates the highest cooling rate within the investigated particle- size fraction: a 0.10 mm particle reaches 100 °C in 0.0115 s, with an average cooling rate of $\approx 6.4 \times 10^4$ °C/s, which is attributed to the predominance of the magnesium matrix with lower specific density.

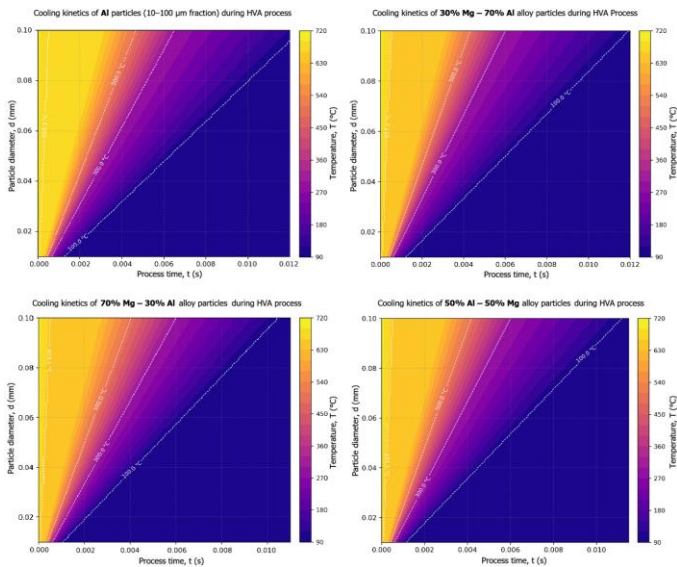


Fig. 5. Modeling results: Dependence of the cooling rate of hydrovacuum- atomized particles of aluminum and Al–Mg alloys on dispersion duration and particle size - fraction 10–100 μ m.

In all cases, a reduction in particle diameter within the investigated range from 100 μ m to 10 μ m leads to an increase in cooling rate by approximately a factor of 10–12.

This allows us to conclude that using the 10–100 μ m fraction during hydrovacuum atomization of Al–Mg alloys enables the stable attainment of ultra- high cooling rates on the order of $10^4 - 10^5$ °C/s, thereby creating favorable conditions for the formation of fine- crystalline, highly heterogeneous, metastabilized substructures in the resulting powders.

This trend is confirmed by the experimental data presented in Fig. 6.

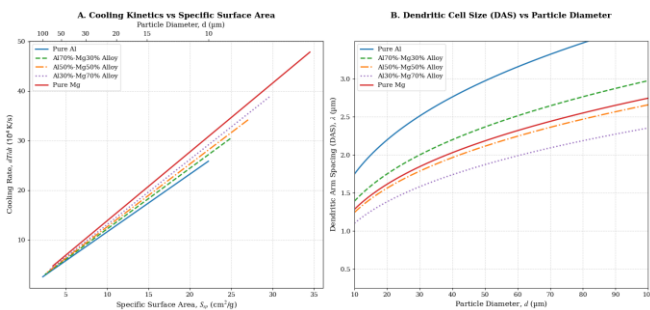


Fig. 6. Influence of the specific surface area of powder particles and their diameter on the cooling kinetics and the size of the resulting dendritic cells.

As seen in Fig. 6, a reduction in particle size from 100 μ m to 10 μ m and an increase in specific surface area from 2–3 to 25–35 cm²/g lead to a pronounced rise in cooling rate (diagram A), which in turn results in a refinement of the dendritic cell size from 2.5–3.0 μ m down to 1.2–1.6 μ m (diagram B).

In binary Al–Mg alloys (particularly in compositions Al 50% – Mg 50% and Al 30% – Mg 70%), the combined effects of constitutional supercooling and segregation processes produce a more dispersed dendritic structure compared to the pure components.

For fine powder fractions ($d < 50$ μ m), the formation of an ultra- fine microstructure (< 2.5 μ m) is reliably ensured, which predetermines a high degree of thermodynamic nonequilibrium and metastable structural state in the resulting powders.

Quenching from the liquid state stabilizes metastable phases and supersaturated solid solutions characterized by a high level of excess internal energy (Gibbs energy).

This substantially reduces both the thermodynamic and kinetic barriers for hydrogen–material interaction, lowering the activation energy of chemisorption.

The extreme cooling kinetics generate a high- density defect structure (high concentrations of vacancies, dislocations, and microstrains).

Local lattice distortions facilitate the incorporation of hydrogen atoms into tetrahedral and octahedral interstitial sites, while microscale segregation and phase heterogeneity create localized regions with increased chemical affinity toward hydrogen.

As a result, hydrogen absorption proceeds with high kinetics at reduced temperatures and pressures. Moreover, in the case of repeated hydrogenation of powders previously dehydrogenated by conventional methods, no prolonged high- temperature, mechanical, or catalytic activation is required, since the metastable structural state remains preserved.

A comprehensive, integrated analysis of the obtained data shows that the key factor governing the kinetics of the phase transition and the resulting metastabilized morphogenesis of powder particles is the coupled influence of the latent heat of crystallization (L_f), which depends on density (ρ), and the melt superheating ($\Delta T = T_{liq} - T_{lic/sol}$), which in turn is determined by the actual melt preparation temperature (T_{liq}) prior to the onset of HVA.

For example, according to numerical thermodynamic modeling, the anomalously high latent heat of crystallization of aluminum ($L_f = 397\,000$ J/kg), combined with the elevated specific heat capacity of its solid phase ($c_{p,sol} = 900$ J/(kg·K)), substantially prolongs the overall solidification duration of a droplet compared with other metallic systems.

In particular, when compared with a magnesium matrix, which possesses a similar latent heat ($L_f = 370\,000$ J/kg) and even higher specific heat capacity ($c_{p,sol} = 1020$ J/(kg·K)), the calculated time required for complete cooling of aluminum particles down to 100 °C is significantly longer ($t_{100^\circ C} = 0.12345$ s vs. 0.08182 s for magnesium, Fig. 4).

This behavior is explained by the substantial difference in density between the compared molten metals (2375 kg/m³ vs. 1570 kg/m³). The higher density of aluminum results in a proportionally greater droplet mass at an equal diameter d (mm), which leads to a significantly larger volumetric heat- storage capacity ($\rho \cdot L_f$ and $\rho \cdot c_p$).

As a consequence, the specific surface area available for heat removal per unit mass ($A/m = 4\pi r^2 / \rho V$) is lower for aluminum, which ultimately prolongs both the phase- transition processes and subsequent cooling. This trend is reflected in Fig. 6A (blue curve).

Additionally, the melt- superheating factor (ΔT) makes a substantial contribution.

A high melt- preparation temperature T_{liq} generates a significant excess of thermal energy in the liquid phase ($Q_{overheat} = m \cdot c_{p,liq} \cdot \Delta T$), which must be dissipated before the onset of solidification.

In combination with the high volumetric heat capacity of aluminum ($\rho \cdot c_p$) and its latent heat (L_f), this leads to an overall

increase in the thermal inertia of the droplet and explains the pronounced prolongation of the time required for complete cooling ($t_{100^\circ\text{C}}$). Consequently, aluminum exhibits a comparatively coarse dendritic structure (cell sizes $> 3 \mu\text{m}$, Fig. 6B, blue curve).

On the other hand, the large magnitude of the phase enthalpy reflected in the latent heat of crystallization (L_f), when combined with extreme convective–radiative heat extraction, creates unique conditions for the quasi- instantaneous fixation of strongly nonequilibrium substructures.

The latent heat released during aluminum crystallization briefly maintains high matrix plasticity within the temperature interval of the phase transition. Against the background of continuous ultrasonic shock- wave loading from the HVA medium, this promotes the intensive development of shear deformations, the generation of dislocation ensembles, and the stabilization of a pronounced “spongy” porosity throughout the volume of the forming powder particle (Fig. 7).

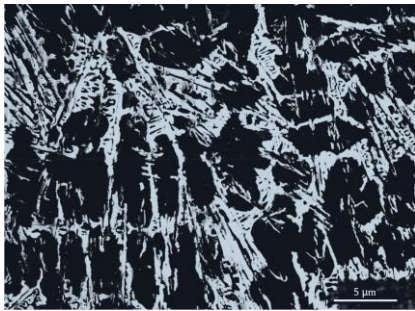


Fig. 7. Microsection of a particle produced by hydrovacuum atomization from the Al–Mg alloy (Al 70% – Mg 30%), particle from the 100 μm fraction.

Since, in the HVA process, the primary adjustable parameter governing the cooling (and, accordingly, supercooling) regime is the degree of initial superheating of the melt supplied for atomization, it can be stated that targeted control of this parameter enables regulation of the actual residence time of the dispersed fragment in both the liquid and the transitional liquid–crystalline states. This residence time is critically important for structural formation, activation, and the degree of hydrogenation.

It is noteworthy that, in the case of Al–Mg and other binary alloys possessing a defined solidification interval, an equally important control criterion becomes the establishment of an optimal balance between the melt- superheating level and the temperature range (interval) of crystallization (as determined from phase diagrams).

As demonstrated by the experimental results, this factor acts as the key technological lever in the combined processes of structure formation and hydrogenation (Figs. 8 and 9).

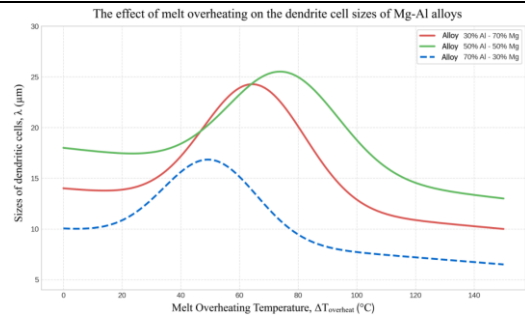
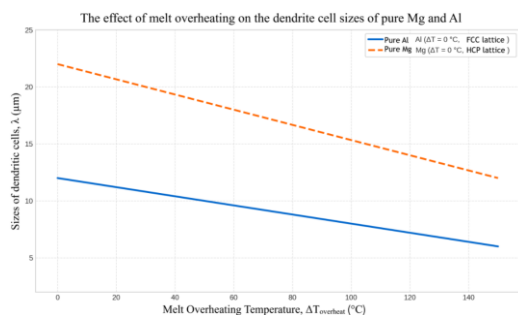


Fig. 8. Influence of melt superheating on the size of dendritic cells.

High melt superheating reduces melt viscosity and surface tension, which, under hydrovacuum atomization, ensures finer droplet fragmentation and an increased cooling rate.

Since pure metals do not exhibit complex eutectic transformations or a dendrite- forming interval ($T_{\text{lic}} \approx T_{\text{sol}}$), a simple direct inverse relationship is observed: - the higher the superheating, the finer the resulting structure.

Pure magnesium, due to the characteristics of its hexagonal close- packed lattice and its stronger tendency for directional crystal growth, initially exhibits a coarser grain size than pure aluminum with its face- centered cubic lattice; however, the overall trend of the curves for both metals remains descending.

In contrast to pure metals, binary Al–Mg alloys possess a wide solidification interval ($\Delta T > 0$), which is determined from the phase diagram.

Within the range of moderate superheating (typically around 50–80 $^\circ\text{C}$), the curve shows a pronounced rise, - an increase in the average grain size (the peak region).

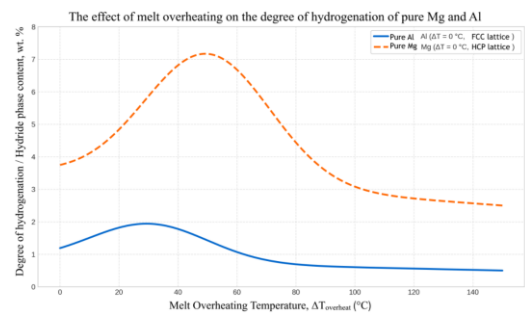
This behavior is associated with the persistence of nucleating microclusters in the melt and enhanced liquation (component segregation), both of which promote the coarsening of dendritic structures during solidification.

Compositions enriched in magnesium or located near the eutectic exhibit a wider solidification interval, which makes the grain- coarsening peak more pronounced.

The aluminum- rich alloy (70% Al, 30% Mg — blue dashed line) has a narrower solidification interval and correspondingly smaller grain- size values.

Notably, when the melt- superheating temperature exceeds a critical threshold (100–120 $^\circ\text{C}$), all inherited micro- inhomogeneities and clusters are completely destroyed.

The melt becomes fully homogeneous, which under subsequent rapid cooling allows the solidification interval to be traversed with suppressed grain growth, ensuring the formation of minimal grain sizes in the final powder.



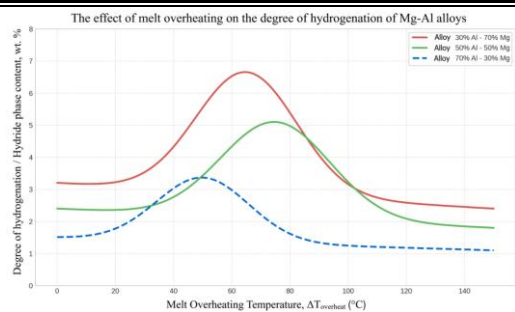


Fig. 9. Influence of melt superheating on the degree of hydrogenation.

Alloys with high magnesium content (70%) exhibit the strongest tendency to interact with hydrogen and to form metastable MgH_2 phases, showing the highest hydrogenation degrees. Alloys with 50% Mg contain a well- developed eutectic component and a highly defective microstructure at moderate superheating, forming a pronounced peak. Aluminum- rich alloys (30% Mg), due to the partial protective influence of finely dispersed nanoporous aluminum- oxide films, demonstrate the lowest hydrogenation values.

However, aluminum is not a passive component; on the contrary, it actively participates in hydrogen chemisorption, forming surface Al-H complexes and promoting hydrogen redistribution within the solid phase.

The thermodynamic stability of aluminum and its higher Al-H bond energy partially “counterbalance” the excessive reactivity of magnesium, weakening Mg-H interactions and facilitating reversible low- temperature dehydrogenation, - a particularly important factor for cyclic processes.

This behavior is confirmed by the X- ray diffraction data illustrated in Fig. 10.

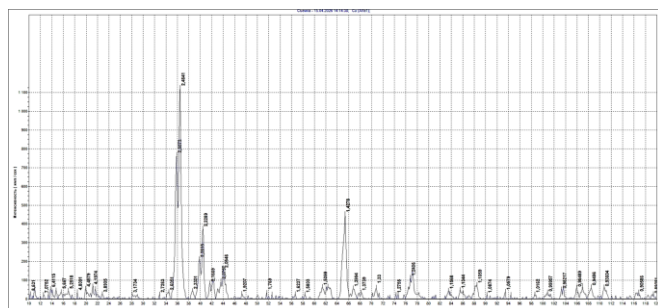


Fig. 10. X- ray diffraction pattern of the atomized Al-Mg alloy powder (70% Mg – 30% Al).

The presented X- ray diffraction pattern shows that the investigated sample exhibits well- defined, intense diffraction peaks corresponding to the coexistence of crystallographic phases of the initial metallic components (magnesium and aluminum), as well as the products of their interaction with hydrogen.

The presence of distinct reflections confirms the formation of the magnesium hydride phase MgH_2 , along with stable intermediate structures and surface Al-H complexes, which directly correlate with hydrogen redistribution processes within the solid phase.

The presence of characteristic peaks with well- defined interplanar spacings reflects the high degree of dispersity and defectiveness of the crystalline structure, which is governed by the developed eutectic component and the influence of protective nanoscale oxide films.

These structural features subsequently reduce the overall energy required for reversible activation and enable low- temperature reversible dehydrogenation of the alloy.

In particular, magnesium constitutes the primary component of the matrix structure. The most intense analytical peak is recorded at $2\theta = 36.43^\circ$ ($d = 2.4641 \text{ \AA}$, relative intensity 100%, contributing ~21.78% to the volumetric phase content). High- angle magnesium reflections are observed at $2\theta = 106.95^\circ$ ($d = 0.9585 \text{ \AA}$), 108.41° ($d = 0.9496 \text{ \AA}$), and 110.75° ($d = 0.9360 \text{ \AA}$).

Aluminum, in turn, participates in forming the structural framework of the alloy. A characteristic aluminum peak is detected at $2\theta = 65.29^\circ$ ($d = 1.4278 \text{ \AA}$, intensity 288 imp/s, mass fraction ~12.85%), as well as at $2\theta = 38.61^\circ$ ($d = 2.3301 \text{ \AA}$).

The intermetallic compounds $\text{Al}_{12}\text{Mg}_{17}$ and AlMg_3 represent products of alloying and eutectic solidification. The $\text{Al}_{12}\text{Mg}_{17}$ phase is identified at $2\theta = 65.29^\circ / 88.29^\circ$ ($d = 1.1059 \text{ \AA}$), while AlMg_3 appears at $2\theta = 21.15^\circ$ ($d = 4.1974 \text{ \AA}$).

The presence of these phases confirms the well- developed eutectic structure of the alloy.

Diffraction peaks corresponding to AlH_3 are registered in the medium- and high- angle regions at $2\theta = 41.64^\circ$ ($d = 2.1669 \text{ \AA}$), 52.55° ($d = 1.7400 \text{ \AA}$), 61.35° ($d = 1.5099 \text{ \AA}$), and within the $83\text{--}106^\circ$ range ($2\theta = 83.49^\circ, 85.54^\circ, 93.45^\circ, 105.93^\circ$).

This confirms that aluminum is not inert but actively participates in hydrogen chemisorption, forming surface Al-H complexes.

Characteristic reflections of orthorhombic MgH_2 (typically strong peaks at $2\theta \approx 27.9^\circ, 35.7^\circ, 38.2^\circ$, and 39.9°) appear near the magnesium peaks; however, in the experimental diffractogram they merge into broadened composite peaks due to the nanoscale grain state, — high defect density and small crystallite thickness ($17\text{--}19 \text{ nm}$).

The recorded significant peak half- width ($0.4639^\circ \approx 0.0081 \text{ rad}$) combined with high intensity ($I = 734 \text{ imp/s}$) indicates not amorphization but pronounced subgrain fragmentation and a high dislocation density, both induced by the extreme thermal gradients inherent to hydro-vacuum atomization.

Hydroxide-hydride complexes ($\text{AlH}_3 \cdot \text{O}_3$) are also present in the diffractogram, appearing in the low- angle region at $2\theta = 13.80^\circ$ and 14.73° , reflecting the specific surface interactions of moisture/oxygen with the forming hydride structures.

Notably, the intermetallic $\text{Al}_{12}\text{Mg}_{17}$ reflection at $2\theta = 65.29^\circ$ ($d = 1.4278 \text{ \AA}$) exhibits a peak half- width of 0.6971° , corresponding to an ultrafine crystallite size of approximately $14\text{--}15 \text{ nm}$.

For the oxide phase periclase (MgO), the half- width at $2\theta = 35.78^\circ$ is 0.4407° , while for Al_2O_3 at $2\theta = 39.83^\circ$ it is 0.4272° .

These small coherent- scattering domain sizes confirm the formation of protective nanoporous oxide frameworks.

The maximum peak broadening is observed for reflections at $2\theta = 16.87^\circ$ (0.8080° for $\text{Al}_{12}\text{Mg}_{17}$), $2\theta = 62.35^\circ$ (0.9210° for Mg), and $2\theta = 77.07^\circ$ (0.7190°).

Such pronounced broadening at low and medium intensities indicates a high level of type- II microstrains within the crystal lattice, caused by local lattice distortions due to incorporated hydrogen atoms and vacancies.

Thus, the dependencies of λ and the hydrogenation degree on $\Delta T_{\text{overheat}}$, presented in Figs. 8 and 9, consistently demonstrate that the thermodynamically governed evolution of the dendritic- structure scale is the key factor determining the hydrogen- saturation capacity and functional properties of powders produced by hydrovacuum atomization.

5. Generalized semi- empirical model for the formation of crystalline- structure parameters.

Based on the theoretical and experimental data obtained in this study, a semi- empirical generalized expression was developed to mathematically describe the combined influence of melt- superheating temperature and the solidification interval on the resulting structural scale (dendritic- cell or grain size, λ).

The model incorporates three principal factors: 1) Baseline structural refinement driven by increasing superheating ($\Delta T_{\text{overheat}}$); 2) Structural coarsening in the moderate- superheating region, associated with the persistence of micro- inhomogeneities and the

width of the solidification interval ($\Delta T_{\text{interval}}$); 3) An individual component- affinity coefficient, reflecting the tendency of alloy constituents to form clusters or protective films, - in this case, governed by the Al/Mg ratio.

$$\lambda = \lambda_0 \cdot \exp(-\Delta T_{\text{overheat}}/k_1) + A_1 \cdot (\Delta T_{\text{interval}}/T_{\text{ref}}) \cdot \exp(-(\Delta T_{\text{overheat}} - T_{\text{crit}})^2 / 2 \sigma^2) + C \quad (9)$$

Where: λ - resulting dendritic- cell or grain size (μm); λ_0 - initial structural scale of the base pure metal; $\Delta T_{\text{overheat}}$ - melt- superheating temperature above the liquidus ($^{\circ}\text{C}$); $\Delta T_{\text{interval}}$ - alloy solidification interval ($T_{\text{liquidus}} - T_{\text{solidus}}$), defining the width of the phase- transition zone ($^{\circ}\text{C}$); k_1 - thermal- damping coefficient (responsible for monotonic cell narrowing under deep superheating); A_1 - coefficient describing the influence of liquation and inherited clusters (directly proportional to the fraction of components with a wide solidification interval, e.g., 30% Al–70% Mg or 50% Al–50% Mg compositions); T_{crit} - critical moderate- superheating temperature (typically 50–80 $^{\circ}\text{C}$) at which the structural peak (melt heterogeneity) is most pronounced; T_{ref} - reference normalization temperature (100 $^{\circ}\text{C}$); σ - width of the melt- instability peak; C - technological limit of structural refinement under extremely high cooling rates during hydrovacuum dispersion.

The proposed generalized relationship makes it possible to quantitatively describe how the thermodynamic properties of metallic materials influence structure formation during hydrovacuum atomization.

Specifically: – the first exponential term reflects the dominance of thermodynamic factors; as the melt- superheating temperature increases ($\Delta T_{\text{overheat}} \gg k_1$), its viscosity and surface tension decrease exponentially, leading to a monotonic reduction in the dendritic- cell scale (λ).

– the second term, a Gaussian bell- shaped function, describes the “anomalous” structural peak that arises within the moderate- superheating range (T_{crit}), where liquation- induced heterogeneities and cluster groupings persist.

The amplitude and width of this peak are governed by the solidification interval ($\Delta T_{\text{interval}}$): it vanishes for pure metals ($\Delta T_{\text{interval}} \rightarrow 0$), while in Al–Mg alloys it produces a pronounced maximum.

Equation (9), together with the experimental trends shown in Figs. 8 and 9, demonstrates a direct correlation between the dendritic- structure scale λ and the hydrogen- saturation capacity of the particles. For pure metals (Al, Mg), the monotonic decrease in λ with increasing $\Delta T_{\text{overheat}}$ (Fig. 8) leads to a higher fraction of defective boundaries and active surface sites, which manifests as an increased degree of hydrogenation and a higher content of hydride phases (Fig. 9). This effect is especially pronounced for magnesium and Mg- rich systems.

In Al–Mg alloys, the nonlinear, hump- shaped dependence $\lambda(\Delta T_{\text{overheat}})$, governed by the Gaussian term in Equation (9), leads to the fact that within the intermediate- superheating region ($T_{\text{crit}} \approx 50\text{--}80\text{ }^{\circ}\text{C}$), dendritic- cell coarsening is accompanied by a reduction in the effective area of active boundaries and a decrease in the hydride- phase fraction.

Upon transitioning to deep superheating ($>120\text{ }^{\circ}\text{C}$) followed by rapid cooling, λ decreases again, and the structure becomes fine- dispersed and defect- enriched.

This promotes enhanced hydrogen diffusion and uptake, resulting in higher hydrogenation degrees, - particularly in Mg- rich compositions.

According to the derived equation, the resulting dendritic- cell or grain size, being itself dependent on the solidification duration of the particles, directly influences the depth and character of hydrogen uptake. Consequently, the longer a particle remains within the high- temperature transitional solidification interval, the more time is available for sonovolumetric action and condensational sonomorphosis, both of which arise under hydrovacuum

atomization conditions. These effects enhance hydrogen diffusion and capture, stabilize defect- rich states, and generate activated structures capable of sustaining multiple hydrogenation–dehydrogenation cycles.

Taken together, these findings lead to the key conclusion that the thermodynamics of phase transformations, alloy composition, and solidification kinetics jointly determine the efficiency of structure formation and its targeted adaptation to subsequent hydrogenation–dehydrogenation cycles.

This establishes a fundamental basis for developing methods of purposeful design of highly stable functional powders for hydrogen- energy applications.

6. Conclusion

The analysis of the thermodynamic properties of metallic materials, combined with thermal- regime modeling of particle cooling during hydrovacuum atomization, demonstrates that differences in heat capacity, thermal conductivity, and latent heat of fusion generate unique temperature–time cooling trajectories for the produced particles, thereby defining their structural state.

The modeling results, together with data from parallel experimental investigations, establish a closed optimization loop for the technological process: thermodynamic properties $\rightarrow$ thermal history of particles $\rightarrow$ structure formation $\rightarrow$ hydride formation $\rightarrow$ adjustment of melt parameters $\rightarrow$ increased efficiency of atomization and hydrogenation.

This approach enables predictive control over the structural evolution and reactive capability of atomized metallic systems, providing a scientifically grounded platform for designing highly efficient regimes of hydrovacuum processing and hydrogenation.

The constructed thermal maps (isotherms) of particle cooling demonstrate that the parameters t_{sol} and $t_{100^{\circ}\text{C}}$ serve as reliable indicators of solidification and cooling kinetics and can be used to predict the critical intervals of dendritic, highly activated, and therefore hydrogen- intensive structure formation.

It was found that rapidly cooling systems (Mg, Al–Mg alloys) tend to form fine- dispersed, highly defective, and metastable structures, whereas materials with high thermal inertia (Pb, Armco- Fe) retain coarse structural elements and prolonged high- temperature states. This explains their lack of competitiveness compared to the lightweight metals investigated in this study.

It is shown that the reactive (chemisorptive) hydrogen- uptake capability is determined not only by composition but also by the combined thermodynamic properties of the alloy components.

Mg- rich systems (50–70% Mg) indeed exhibit a strong tendency toward hydride formation (MgH_2). However, aluminum, when present alongside magnesium, does not act as a passivating component; rather, it actively participates in hydrogen chemisorption, forming surface Al–H complexes and facilitating hydrogen redistribution within the solid phase.

The thermodynamic stability of aluminum and its higher Al–H bond energy partially offset the excessive reactivity of magnesium, attenuating Mg–H interactions and enabling reversible low- temperature dehydrogenation, a feature of particular importance for cyclic hydrogenation–dehydrogenation processes.

Two scientifically substantiated pathways for the purposeful production of HVA- powders for different applied tasks have been identified.

For obtaining dense, homogeneous particles of globular morphology, eutectic and near- eutectic compositions are optimal, as they ensure the condition $\Delta T_{\text{interval}} \rightarrow 0$, maximize the solidification rate, and minimize the free energy of the system.

For generating metastable, activated structures adapted to repeated hydrogenation–dehydrogenation cycles, alloys with a wide solidification interval ($\Delta T_{\text{interval}} \neq 0$) are preferable, provided that the melt- superheating level $\Delta T_{\text{overheat}}$ is strictly controlled and satisfies the condition $\Delta T_{\text{overheat}} \geq \Delta T_{\text{interval}}$ during the preparation stage prior to hydrovacuum atomization.

Acknowledgments:

This work was financially supported by the Shota Rustaveli National Science Foundation of Georgia (Grant No. FR 25–10112).

The authors express their deep gratitude to their colleagues at the Ferdinand Tavadze Institute of Metallurgy and Materials Science and Georgian technical University — Tamaz Batsikadze and Nikoloz Jalabadze — for their assistance in conducting the research.

References

1. Tizon, J. A., Liu, Y., Akundi, S. S., Braniff, A., Dantas, B., Tian, Y., Khan, F. I., & Pistikopoulos, E. N. (2026). Metal hydride storage systems from a safety perspective: Mechanistic modeling, optimization, and risk-based control. *Journal of Energy Storage*, 171, 122870. <https://doi.org/10.1016/j.est.2026.122870>
2. Wu, Z., Guo, T., Li, X., Liu, H., Wang, B., Yao, J., Yang, F., Zhang, Z., Yuo, J., Grbovic Novakovic, Y., Xing, L., Zhu, P., & Li, Q. (2025). Overview of swelling stress formation and control of metal hydrides for high-safety and high-density hydrogen storage applications. *Applied Energy*, 402(A), 126909. <https://doi.org/10.1016/j.apenergy.2025.126909>
3. Sharma, P. (2026). Metal Hydride-Based Systems and Applications. In: *A Textbook on Hydrogen Energy*. Springer, Singapore. https://doi.org/10.1007/978-981-95-4601-5_17
4. Das, A., Ghosh, A., Bharat, B.S. et al. (2026). Review: next-generation metal hydride systems for sustainable hydrogen storage—kinetics, nanostructuring, and intelligent materials discovery. *J Mater Sci* 61, 17697–17760. <https://doi.org/10.1007/s10853-026-12886-7>
5. Qayyum, M. N., Majid, A., & Raza, M. T. (2026). Solid-state hydrogen storage in metal hydrides: mechanistic insights into kinetics, activation, and destabilization strategies. *RSC Advances*. <https://doi.org/10.1039/d6ra05276b>
6. Larpruenrudee, P., Bennett, N. S., Luo, Z., Hossain, M. J., Haque, N., Sauret, E., Fitch, R., & Islam, M. S. (2025). A review on the overall performance of metal hydride-based hydrogen storage systems. *Energies*, 18(5), 1291. <https://doi.org/10.3390/en18051291>
7. Liu, W., Tupe, J. A., & Aguey-Zinsou, K.-F. (2025). Metal hydride storage systems: Approaches to improve their performances. *Particle & Particle Systems Characterization*, 42(3), 2400163. <https://doi.org/10.1002/ppsc.202400163>
8. Liu, Y., Chabane, D., & Elkedim, O. (2021). Intermetallic compounds synthesized by mechanical alloying for solid-state hydrogen storage: A review. *Energies*, 14(18), 5758. <https://doi.org/10.3390/en14185758>
9. Xu, J., Yang, H., Zhang, W., Shen, A., Liu, J., Zhang, L., Li, Y., Han, S., Ye, Y., Yan, K., & Cheng, H. (2026). Superior hydrogen storage characteristics of LaNi₅ – LaMgNi₄ bi-phase alloys. *Renewable Energy*, 258, 125036. <https://doi.org/10.1016/j.renene.2025.125036>
10. Miniyazov, A. Z., Mukhamedova, N. M., Sokolov, I. A., Tulenbergenov, T. R., Ospanova, Z. N., Uazyrkhanova, G. K., Bekmagambetova, B. Y., Oken, O., & Zhakiya, R. Y. (2025). Structural and phase evolution in the Mg–Al system leading to reduced hydrogen desorption temperature. *Hydrogen*, 6(4), 108. <https://doi.org/10.3390/hydrogen6040108>
11. Haryadi, Suwarno, Guntur, H. L., Zohri, M., Hijriawan, M., & Tolj, I. (2026). Thermodynamic destabilization of Mg- based hydrogen storage materials: A critical review. *Journal of Alloys and Compounds*, 1062, 187572. <https://doi.org/10.1016/j.jallcom.2026.187572>
12. Bartholomew, C.H. (2001). Mechanisms of catalyst deactivation. *Applied Catalysis A-general*, 212, 17-60. [https://doi.org/10.1016/S0926-860X\(00\)00843-7](https://doi.org/10.1016/S0926-860X(00)00843-7)
13. Fiss, B. G., Richard, A. J., Frišić, T., & Moores, A. (2021). Mechanochemistry for sustainable and efficient dehydrogenation/hydrogenation. *Canadian Journal of Chemistry*, 99(2), 94–109. <https://doi.org/10.1139/cjc-2020-0408>
14. Gaybullaeva, Z. Kh., Nasymov, G. T., Asrorov, B. I., & Sharifov, A. (2021). Production of aluminium hydride by plasma chemical catalytic reaction. *Tsvetnye Metally*, (11), 32–38. <https://doi.org/10.17580/tsm.2021.11.04>
15. Merouani S., Dehane A., Hamdaoui O. (2025). Hydrogen production via water ultrasonication: A review. *Ultrasonics Sonochemistry*, 120, 107515. <https://doi.org/10.1016/j.ultsonch.2025.107515>
16. Baidukova O., Möhwald H., Mazheika A. S., Sviridov D. V., Palamarcu T., Weber B., Cherepanov P.V., Andreeva D. V., Skorb E. V. (2015). Sonogenerated metal-hydrogen sponges for reactive hard templating. *Chem. Commun.*, 51 (36): 7606–7609. <https://doi.org/10.1039/c4cc10026c>
17. Troia A., Olivetti E. S., Martino L., Basso V. (2019). Sonochemical hydrogenation of metallic microparticles. *Ultrasonics Sonochemistry*, 55, 1-7, <https://doi.org/10.1016/j.ultsonch.2019.03.004>
18. Sakhvadze D., Jandieri G., Tsirekidze T., and Gorbenko I., “Device for producing metallic powder from melt,” GE Patent P20156384, (2015). <https://patents.google.com/patent/GE20156384B/en>
19. Sakhvadze, D., Jandieri, G., Saralidze, B., & Sakhvadze, G. (2024). A novel method of hydro-vacuum dispersion of metallurgical melts: research and implementation. In *Sediment Transport Research - Further Recent Advances*. IntechOpen. <https://doi.org/10.5772/intechopen.1004129>
20. Jandieri, G. V., Sakhvadze, D. V., Saralidze, B. G. et al. (2024). Physical and Technological Features of Mechanoactivation of Powder Particles Formed during Hydro-Vacuum Dispersion of Metallic Melts. *Physics of Metals and Metallography*, 125, 478–491 <https://doi.org/10.1134/S0031918X23603190>
21. Sakhvadze D, Jandieri G, Sakhvadze G, et al. (2024). Detection of sonochemical hydrogenation effect in the process of hydro-vacuum dispersing of melts and its significance. *Materials Science. Non-Equilibrium Phase Transformations*. 10(1): 8–13. <https://stumejournals.com/journals/ms/2024/1/8>
22. Quéré, D. (2013). Leidenfrost dynamics. *Annual Review of Fluid Mechanics*, 45(1), 197–215. <https://doi.org/10.1146/annurev-fluid-011212-140709>

Study of the influence of the cross-linker on the modification of cotton fabric with chitosan for controlled release of diclofenac and preparation of antimicrobial textiles

Daniela Atanasova
University of Chemical Technology and Metallurgy, Sofia, Bulgaria
d.atanasova@uctm.edu

Abstract: Composite materials with potential application in medical textiles were developed by modifying cotton fabric with chitosan containing diclofenac. The influence of the concentration of citric acid as a crosslinking agent on the properties of the materials was studied. The resulting composite materials were characterized by gravimetric analysis, optical microscopy, contact angle measurement and thermogravimetric analysis. The antimicrobial activity of the cotton samples was evaluated against Gram-positive and Gram-negative model bacterial strains. A synergistic antimicrobial effect of chitosan and diclofenac and a uniform release of diclofenac *in vitro* under physiological conditions were established.

Keywords: MEDICAL TEXTILES, COTTON FABRIC, CHITOSAN, CITRIC ACID, CROSSLINKING, DICLOFENAC, ANTIBACTERIAL ACTIVITY

1. Introduction

Medical textiles are one of the most dynamically developing areas of technical textiles, widely used in modern healthcare. The development of new materials and technologies has significantly expanded the possibilities for creating functional textile products intended for wound treatment, infection control, local delivery of medicinal substances and other medical applications [1, 2]. Among them, wound dressings occupy a special place, which, in addition to a protective function, must provide an optimal environment for tissue regeneration, limit the development of microorganisms and, if necessary, carry out a controlled release of biologically active substances [3].

Cotton fabrics are widely used as a base for medical textiles due to their biocompatibility, good absorbency, air permeability and mechanical strength. Despite these advantages, the lack of intrinsic antimicrobial activity necessitates their surface modification with biologically active polymers [4].

Among natural polymers, chitosan has attracted considerable scientific interest due to its biocompatibility, biodegradability, non-toxicity, film-forming ability and pronounced antimicrobial activity. Due to its reactive amino and hydroxyl groups, it can be chemically crosslinked and used as a carrier for medicinal substances, which allows the development of multifunctional textile materials for wound healing [5]. One of the most promising crosslinking agents is citric acid, which provides stable crosslinked of chitosan on cellulose fibers and can influence the structure, surface properties and functional characteristics of the resulting materials [6].

Despite a significant number of publications, the influence of citric acid concentration on the properties of cotton fabric modified with chitosan containing diclofenac is still insufficiently studied. The present work aims to evaluate the influence of the concentration of the crosslinking agent on the physicochemical characteristics of the developed composite materials and to analyze their suitability for application as functional medical textiles.

2. Materials and methods

Cotton fabric (100% cellulose) was used as the textile substrate. Chitosan, diclofenac sodium as an anti-inflammatory biologically active substance, and citric acid as a crosslinking agent were used to modify it.

2.1. Preparation of composite materials

The experimental procedure was developed based on our previous studies, with the present work introducing a change only in the concentration of the crosslinking agent used [4, 7].

The cotton fabrics were pre-treated by impregnation with aqueous solutions of citric acid (CA) with concentrations of 1 %, 5 % and 10 % w/w chitosan, then dried at room temperature. In parallel, a chitosan solution (2.7 % w/v) was prepared, to which diclofenac sodium was added under continuous mechanical stirring

until a homogeneous mixture was obtained. After homogenization, the solution was left for 2 h, which allowed the separation of air bubbles and ensured uniform formation of the coating. The pretreated textile samples were impregnated with the resulting chitosan solution containing diclofenac and subsequently subjected to a heat treatment at 80 °C, which resulted in crosslinking of chitosan with citric acid and formation of a stable polymer film on the surface of the cellulose fibers. The resulting materials were designated according to the concentration of the crosslinking agent as follows: CHTD1, CHTD5 and CHTD10.

To assess the influence of the degree of crosslinking, all other technological parameters – chitosan and diclofenac concentration, processing time and thermal fixation conditions – were kept constant.

2.2. Methods for the characterization of composite materials

The change in fabric weight following processing was calculated using Equation (1):

$$(1) \text{Weight gain (\%)} = \frac{w - w_0}{w_0} \times 100$$

where w_0 and w represent the weight of the tissue before treatment and after modification and immersion in distilled water and subsequent drying, respectively.

Microscopic images of the textile samples were obtained using a B- 290TB optical microscope (Optika®, Pontenica, Italy), equipped with a high-quality illumination system and the ability to operate at different magnifications. Observations were performed at 4× and 10× magnifications, which allowed visualization of both the general surface structure and finer morphological details.

The thermal behavior of the studied samples was evaluated by thermogravimetric and differential thermal analysis using a STA PT1600 TG-DTG/DSC (LINSEIS Messgeräte GmbH, Selb, Germany). The measurements were performed at a heating rate of 10 °C min⁻¹ in the temperature range from room temperature (20 °C) to 600 °C, in air.

The contact angle of the studied textile samples with distilled water was measured using the sitting drop method, implemented with an optical tensiometer THETA Flow Auto 1, equipped with a Basler acA2500- 60 µm digital camera. The method is based on recording the profile of a water drop placed on the surface of the textile material and subsequent geometric evaluation of the angle formed between the liquid and the solid surface.

The pH value of the prepared solutions was determined with a Hanna Instruments microprocessor pH meter.

In vitro release of the biologically active substance

The release of diclofenac sodium from the three composite materials obtained using 1%, 5% and 10% citric acid as a crosslinking agent was studied *in vitro* in phosphate buffer with a

concentration of 0.01 M and pH = 7.4 at a temperature of 37 ± 0.5 °C. The amount of diclofenac released was determined spectrophotometrically by measuring the absorption at a wavelength of 277 nm with a UV-Vis spectrophotometer ONDA UV-31SCAN in the range of 190–1100 nm. Each sample was immersed in 20.0 mL of the buffer solution, and at predetermined time intervals 5.0 mL of the medium were taken and replaced with an equal volume of fresh buffer, tempered to 37 °C. The concentration of the released active substance was determined by a previously established calibration curve.

Antimicrobial activity

The antimicrobial properties of the three composite materials were evaluated against representative Gram-positive and Gram-negative bacterial strains – *Bacillus cereus* and *Pseudomonas aeruginosa*. The study was conducted by contacting textile samples with a size of 10×10 mm with bacterial suspensions in sterile meat-peptone broth. Untreated cotton fabric and bacterial medium without textile material were used as control samples.

After incubation of the samples at 28 °C for 18 h with stirring at a speed of 240 rpm, bacterial growth was assessed spectrophotometrically by measuring the optical density of the medium at 600 nm (OD_{600}). The antimicrobial effectiveness of the materials was determined by comparative assessment of the bacterial cell density compared to the control samples. The tests were conducted in three independent replicates, and the influence of the concentration of citric acid on the antimicrobial activity of the resulting composite materials was monitored.

3. Results and Discussion

Gravimetric analysis revealed a gradual increase in the mass of the modified materials with increasing citric acid concentration – from 21.42% for CHTD1 to 22.33% for CHTD10. The observed trend can be associated with an increase in the amount of fixed chitosan layer on the cellulose fibers due to more intensive crosslinking at higher citric acid concentrations.

Figure 1 shows optical micrographs of untreated cotton fabric (CO) and the composite material CHTD10, obtained at $4\times$ and $10\times$ magnifications. In the untreated textile sample, the characteristic configuration of the fibers for the woven structure is observed, forming free spaces in the interweaving zones. The individual cellulose fibers are clearly distinguishable, with characteristic fibrillar structures standing out on their surface. In the modified sample CHTD10, significant morphological changes are observed. At $4\times$ magnification, a formed chitosan coating is observed on the surface of the fibers, while at $10\times$ a dense polymer layer is visualized, which covers the fibers and partially fills the spaces between the individual fibers [8].

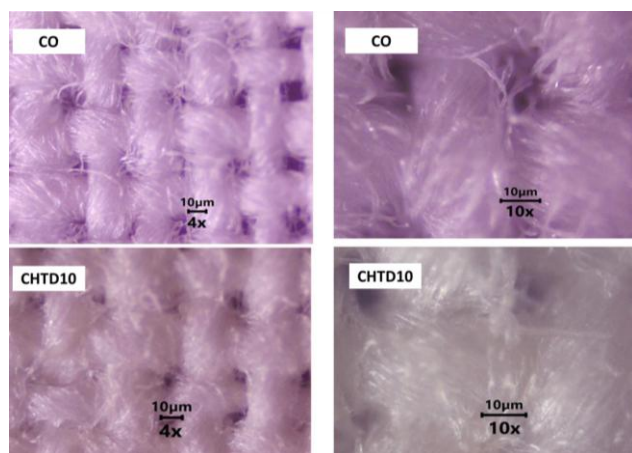


Fig. 1 Optical microscope micrographs of cotton fabric (CO) and composite material CHTD10 (magnification of the photos is $4\times$ and $10\times$).

The thermogravimetric analysis (TGA) and its first derivative – differential thermogravimetric (DTG) curve of the starting cotton fabric and the composite materials CHTD1, CHTD5, and CHTD10 are presented in Fig. 2A and Fig. 2B, respectively. It can be seen that the thermal degradation of all samples proceeds in three stages. After the initial small loss in the weight of the materials at 119 °C, which is due to the release of moisture from the materials (4 % for the untreated cotton fabric, 5.0 % for CHTD1, 5.5 % for CHTD5 and 8.1 % for CHTD10). The second stage is with the most significant thermal degradation, as for the starting cotton fabric it starts at 271 °C (CO - 5.85 %), and for the composite materials at a lower temperature of 234 °C, due to the presence of acids causing degradation of chitosan and cellulose [9]. Respectively for the materials 6.6 % for CHTD1, 8.9 % for CHTD5 and 10.8 % for CHTD10. The mass loss at 370 °C is 73.9 % for CO, 66.7 % for CHTD1, 68.2 % for CHTD5 and 69.3 % for CHTD10. The first derivative also shows that the inflection points for the starting material CO are at 335 °C, for CHTD1 it is at 336 °C, for CHTD5 it is at 337 °C and for CHTD10 it is at 335 °C (Fig. 2B). At 600 °C without leaving dry residues, while the cotton fabric burns at 100 %, and for samples CHTD1, CHTD5 and CHTD10 the dry residues are 15.1 %, 12.4 % and 7.2 %, respectively. With increasing citric acid concentration, a gradual decrease in the residual mass after thermal degradation is observed – from 15.1% for CHTD1 to 7.2% for CHTD10, which indicates a dependence of the thermal behavior on the concentration of the crosslinking agent.

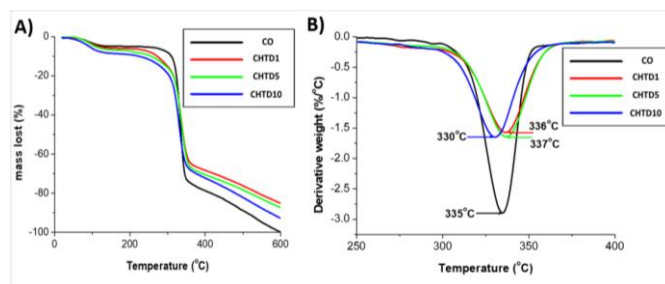


Fig. 2 (A) TG and (B) DTG curves of untreated cotton fabric (CO) and composite materials (CHTD1, CHTD5, and CHTD10).

Figure 3 shows the contact angle values of the composite materials CHTD1, CHTD5 and CHTD10. The original cotton fabric is not included in the figure, since due to its pronounced hydrophilicity, the water droplet is absorbed directly by the surface and a value of 0° is recorded [10]. For the modified materials, values of 91.57°, 92.28° and 94.22° were measured, respectively, and a gradual increase in the contact angle with increasing citric acid concentration was found. The results obtained show a change in the surface wettability of the cotton fabric as a result of the modification, with all the studied composite materials exhibiting a hydrophobic character.

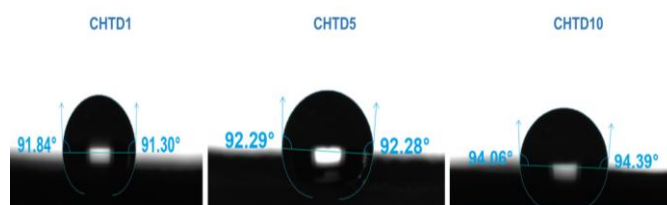


Fig. 3 Evaluation of hydrophilic-hydrophobic properties by measuring the contact angle of wetting with water on composite materials (CHTD1, CHTD5, and CHTD10).

Figure 4 shows the cumulative release profile of diclofenac sodium from samples CHTD1, CHTD5 and CHTD10 in phosphate buffer with pH = 7.4 at 37 °C for 26 hours. During the first 6 hours, a more intensive release of the drug substance from the studied composite materials was established, with the amounts reached being $93.28 \mu\text{g cm}^{-2}$ for CHTD1, $107.82 \mu\text{g cm}^{-2}$ for CHTD5 and 112.98

$\mu\text{g cm}^{-2}$ for CHTD10, respectively. This initial faster stage is probably associated with the desorption of diclofenac located near or on the surface of the materials. After the initial phase of more intensive release, a gradual and more uniform release of diclofenac from the composite matrices was observed until the end of the study period. After 26 hours, the cumulative released amount reached $109.95 \mu\text{g cm}^{-2}$ for CHTD1, $127.52 \mu\text{g cm}^{-2}$ for CHTD5 and $136.07 \mu\text{g cm}^{-2}$ for CHTD10. The observed differences between the individual samples can be related to the peculiarities of the structure and degree of crosslinking of the hydrogel matrix, the way of distribution and retention of the drug substance in it, as well as the processing conditions of the textile materials. These factors determine the accessibility of diclofenac to the aqueous environment and, accordingly, influence the rate, amount and duration of its release.

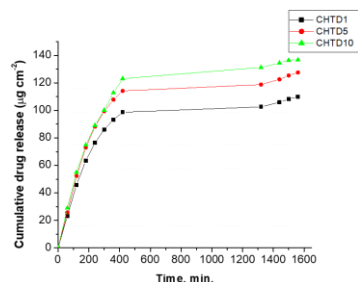


Fig. 4 Release of diclofenac in phosphate buffer (pH=7.4) at 37 °C from composite materials (CHTD1, CHTD5, and CHTD10).

Figure 5 shows the results of the study of the antimicrobial activity of the composite materials CHTD1, CHTD5 and CHTD10 against A) *P. aeruginosa* and B) *B. cereus*, with the untreated cotton fabric (CO) included for comparison. The control sample showed 100% bacterial contamination, with no antimicrobial activity noted. For *P. aeruginosa*, the bacterial reduction for CHTD1, CHTD5 and CHTD10 was 98.6%, 98.4% and 98.0%, respectively, and for *B. cereus* – 98.0%, 97.5% and 98.2%. The high antimicrobial activity is probably due to the combined action of chitosan and diclofenac, as well as to the changes in the surface characteristics of the modified textile materials. The obtained bacterial reduction values are higher than those found for the materials previously studied by us, containing indomethacin and diclofenac. This highlights the potential of the developed composites for application as antimicrobial materials for medical textiles [4,7, 11].

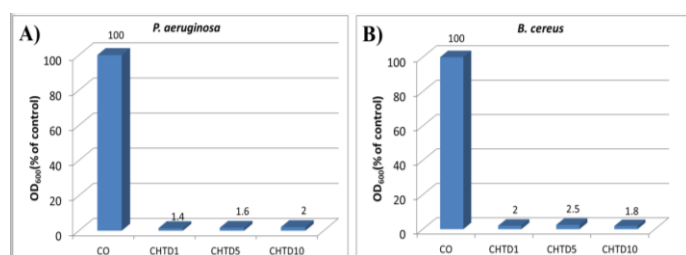


Fig. 5 Fig.5 Antimicrobial activity of cotton fabric (control) and composite materials: CHTD1, CHTD5, and CHTD10 on the growth of A) *P. aeruginosa* and B) *B. cereus*.

4. Conclusion

New composite textile materials were obtained by modifying cotton fabric with chitosan, diclofenac and different concentrations of citric acid. It was found that the concentration of the crosslinking agent affects the mass growth, surface properties and thermal behavior of the materials. All three composites showed high antimicrobial activity against Gram-positive and Gram-negative bacteria, with a bacterial reduction of over 97%. The obtained results define the developed materials as a promising basis for functional medical textiles with potential application in wound dressings and controlled release of diclofenac.

5. References

1. M.B. Motlagh, A. Azarniya, A.A. Merati, Woodhead Publishing: Cambridge, (2023)
2. Z. Liu, F. Yin, N. Ruan, Z. Gao, Medicine, **102(45)**, e35956 (2023)
3. N. Gogoi, S. Bhuyan, Medical textiles: it, s present and prospects. Pharma Innovation J, **9(9)**, 160-163, (2020)
4. D. Atanasova, D. Staneva, J. Chem. Technol. Metall. **60(6)**, 1015-1022, (2025)
5. C. Ardean, C.M. Davidescu, N.S. Nemeş, A. Negrea, M. Ciopec, N. Duteanu, P. Negrea, D. Duda-Seiman, V. Musta, Int. J. Mol. Sci., **22**, 7449, (2021)
6. N. Sharmin, J.T. Rosnes, L. Prabhu, U. Böcker, M. Sivertsvik, Molecules, **27**, 5118, (2022)
7. D. Atanasova, D. Staneva, J. Chem. Technol. Metall. **60(6)**, 995-1004, (2025)
8. D. Staneva, D. Atanasova, D. Angelova, P. Grozdanov, I. Nikolova, I. Grabchev, Materials, **16**, 5090, (2023)
9. H.Y. C.-Eulalio, J.F. B.-Rodrigues, K. O.-Santos, C. Peniche, M. V.-LiaFook, Rev. Cuba. Quím., **31(3)**, 309-323, (2019)
10. L. Liang, M.J. Lis Arias, Z. Lou, Q. Mao, C. Ye, X. Meng, J. Eng. Fibers Fabr., **14**, 1-9, (2019)
11. D. Atanasova, D. Staneva, I. Grabchev, IOP Conf. Ser. Mater. Sci. Eng., **1188(1)**, 012004, (2021)

Integrated comparative assessment of material, energy and construction-time efficiency of prefabricated and conventional reinforced concrete systems

Veis Šerifi¹, Nazim Manić¹, Emir Maslak¹ and Vesnera Šerifi²

¹ State University of Novi Pazar, Department of Technical and Technological Sciences, Faculty of Civil Engineering, Novi Pazar, Serbia²

University of Pristina, Faculty of Technical Sciences, Architecture, Kosovska Mitrovica
serifiveis@np.ac.rs, nmanic@np.ac.rs, emaslak@np.ac.rs, vesneraserifi@outlook.com

Abstract: The selection of an appropriate structural and construction system significantly influences material consumption, energy demand, construction duration and overall project efficiency. This study presents an integrated parametric methodology for comparing prefabricated and conventional cast-in-situ reinforced concrete systems under equivalent functional and structural requirements. A representative five-storey building with a gross floor area of approximately 5,000 m² is analysed using two construction scenarios: CIS (conventional cast-in-situ reinforced concrete) and PRE (prefabricated reinforced concrete). The assessment incorporates concrete and reinforcement consumption, material losses, structural construction duration, embodied energy of principal materials, additional production energy, transportation and site energy. The analysed performance dimensions are integrated into a dimensionless Construction Efficiency Index (CEI), while sensitivity analysis evaluates the influence of decision priorities. At a reference factory-to-site distance of 50 km, the parametric scenario indicates a reduction of approximately 7.8% in total structural-material input, 25% in structural construction duration and 6.2% in total energy demand for PRE relative to CIS. The baseline CEI increases from 1.000 for CIS to 1.153 for PRE. The study additionally introduces a project-specific break-even transportation-distance model. Under the adopted assumptions, the energy advantage of prefabrication disappears at approximately 185 km, whereas the integrated CEI advantage persists to a substantially larger theoretical distance because material and time benefits remain. The proposed framework demonstrates that prefabrication should not be evaluated through a single indicator. Its relative advantage depends on the combined effects of materials, energy, time and logistics. The methodology is intended as an early-stage engineering decision-support approach and requires project-specific inventory data for application to real construction projects.

KEYWORDS: PREFABRICATED CONSTRUCTION; REINFORCED CONCRETE; MATERIAL EFFICIENCY; EMBODIED ENERGY; CONSTRUCTION TIME; TRANSPORT; CONSTRUCTION TECHNOLOGY; CONSTRUCTION EFFICIENCY INDEX.

1. Introduction

The construction sector is increasingly required to improve resource efficiency, reduce environmental impacts and shorten project delivery periods while maintaining structural performance, quality and durability. In this context, industrialised and prefabricated construction methods have gained significant attention as alternatives to conventional cast-in-situ construction. Their principal distinction lies in transferring a considerable part of the production process from the construction site to a controlled factory environment, followed by transportation and assembly of prefabricated components on site. This change in production logic affects material consumption, labour organisation, construction time, energy demand, transportation requirements and the generation of construction waste [3].

Reinforced concrete remains one of the dominant structural materials in multi-storey buildings, and both conventional cast-in-situ and prefabricated concrete systems rely heavily on concrete and reinforcing steel. However, the distribution of material and energy inputs differs considerably between the two construction approaches. Prefabrication can provide improved production control and reduce certain on-site activities, but it may simultaneously require additional energy for factory processing, lifting and transportation of large structural elements. Recent life-cycle research therefore supports stage-by-stage comparison rather than simplified assumptions about overall environmental superiority [1].

Material efficiency represents one of the principal criteria for comparing alternative construction systems. Factory-based production can potentially improve dimensional control, standardisation and material utilisation, while reduced dependence on temporary formwork and repeated on-site operations may decrease certain categories of construction waste. Nevertheless, prefabrication does not automatically result in lower consumption of all structural materials. Comparative life-cycle studies have shown that specific prefabricated projects may consume more concrete or reinforcing steel than comparable cast-in-situ solutions, depending on structural configuration, prefabrication rate and component design [2]. Consequently, material efficiency should be evaluated quantitatively for the specific structural system rather than assumed as an inherent advantage of prefabrication.

Construction duration is another important factor. The separation of factory production from on-site preparation enables certain activities to be performed in parallel and can reduce the duration of on-site structural works. Previous life-cycle assessments of prefabricated buildings have identified shorter construction periods among the potential advantages of industrialised construction, although the realised benefit depends on project organisation, production capacity, logistics and assembly efficiency [3]. Therefore, construction-time comparison should consider the complete delivery process rather than only the final on-site erection phase.

The environmental and energy implications of prefabrication are more complex. Embodied energy associated with construction is distributed among material production, component fabrication, transportation, site activities and equipment operation. Abey and Anand compared the embodied energy of prefabricated and conventional residential construction and showed that energy-intensive materials dominate both systems, while transportation may become a significant component when prefabricated elements are produced far from the site [4]. Their case study illustrates that prefabrication should not automatically be assumed to provide an energy advantage under all project conditions.

Conversely, other comparative studies have reported lower environmental impacts for prefabricated construction. Mao et al. found lower construction-stage greenhouse-gas emissions for a semi-prefabricated residential alternative, although transportation of prefabricated components partly offset the achieved reduction [5]. Wang et al. also reported favourable life-cycle energy and cost performance for the prefabricated building examined in their case study [3]. These contrasting findings indicate that relative performance is highly dependent on system boundaries, material quantities, component production methods, transportation distances and project-specific assumptions.

Transportation is therefore a particularly important parameter in the assessment of prefabricated reinforced-concrete systems. Unlike conventional construction, in which raw materials or ready-mixed concrete may often be supplied from relatively local sources, prefabricated construction requires the transport of completed structural elements whose mass and dimensions may result in considerable logistics-related energy consumption. Recent carbon-footprint research similarly

identifies material production and transportation as important contributors to the life-cycle impacts of prefabricated buildings [6].

This relationship suggests that transportation distance may represent a decisive variable when selecting between construction systems. For a sufficiently short distance between the prefabrication plant and the construction site, reductions in site energy, waste and construction duration may outweigh the additional transport requirement. As transport distance increases, however, the energy associated with moving prefabricated components also increases and may progressively reduce or eliminate the overall energy advantage.

The present study therefore introduces the concept of a project-specific break-even transportation distance, representing the transport distance at which the total energy performance of the prefabricated alternative becomes equivalent to that of the corresponding conventional system. The break-even value is not treated as a universal constant because it depends on component mass, vehicle characteristics, transport-energy intensity and the initial energy difference between the compared systems.

Another methodological challenge is that material efficiency, energy consumption and construction duration are expressed in different physical units and may lead to conflicting conclusions. A prefabricated system may provide a substantial reduction in construction time while exhibiting only a marginal improvement, or even a disadvantage, in embodied energy. Accordingly, the objective of this study is to develop an integrated comparative methodology for evaluating the material, energy and construction-time efficiency of prefabricated and conventional

reinforced-concrete systems. The principal scientific contribution is twofold: development of a dimensionless Construction Efficiency Index (CEI), and formulation of a project-specific break-even transportation-distance model for prefabricated reinforced-concrete construction.

2. Methodology

2.1. Research Framework

The methodology was developed to provide an integrated comparison between conventional cast-in-situ reinforced-concrete construction (CIS) and prefabricated reinforced-concrete construction (PRE) under equivalent functional and structural requirements. The analysis considers material efficiency, energy efficiency and construction-time efficiency. The resulting indicators are integrated into a dimensionless Construction Efficiency Index, while a separate transport-distance sensitivity model evaluates the logistical conditions under which prefabrication retains an energy advantage.

2.2. Definition of the Reference Building

A representative five-storey reinforced-concrete building, denoted G+4, was adopted as the reference case. The assumed gross floor area is 5,000 m², or approximately 1,000 m² per storey. The same architectural function and equivalent load-bearing requirements are assumed for both construction alternatives. The comparison focuses on the load-bearing superstructure; components assumed to be identical in both alternatives, such as finishes and building services, are excluded from the comparative calculation.

Table 1. Principal characteristics of the reference building

Parameter	Adopted value
Number of storeys	G+4
Gross floor area	5,000 m ²
Approximate floor area per level	1,000 m ²
Primary structural material	Reinforced concrete
Scenario 1	CIS – Cast-in-situ RC
Scenario 2	PRE – Prefabricated RC

2.3. Material Consumption Assessment

The principal permanent structural materials considered in the analysis are concrete volume V_c and reinforcement mass M_s . Material losses generated during production, transport and construction are considered separately so that the total structural-material resource input includes both installed material and expected losses.

$$M_{str,j} = \rho_c V_{c,j} + M_{s,j} \quad (1)$$

$$M_{res,j} = M_{str,j} + M_{w,j} \quad (2)$$

$$L_{m,j} = (M_{w,j} / M_{res,j}) \times 100 \quad (3)$$

The material-efficiency indicator is defined relative to the conventional CIS system. Values above 1.00 for PRE indicate a lower total structural-material resource input than the reference conventional alternative.

$$I_{M,j} = M_{res,CIS} / M_{res,j} \quad (4)$$

2.4. Construction-Time Assessment

Construction-time analysis is limited to the structural superstructure phase. The relative time reduction and corresponding time-efficiency indicator are defined as follows:

$$R_T = (1 - T_{PRE} / T_{CIS}) \times 100 \quad (5)$$

$$I_{T,j} = T_{CIS} / T_j \quad (6)$$

2.5. Embodied-Energy Assessment

The total energy demand associated with each construction scenario is divided into the embodied energy of structural materials, additional component-production energy, transportation energy and construction-site energy. This formulation is intended to represent a redistribution of energy demand rather than assume that prefabrication necessarily reduces every energy component.

$$E_{tot,j} = E_{mat,j} + E_{prod,j} + E_{tr,j} + E_{site,j} \quad (7)$$

$$E_{mat,j} = M_{c,j} e_c + M_{s,j} e_s \quad (8)$$

$$E_{tr,j} = \sum (M_{k,j} d_{k,j} e_{tr,k} \lambda_k) \quad (9)$$

$$E_{tr,PRE} = M_{PRE} d_{PRE} e_{tr} \lambda \quad (10)$$

$$E_{site} = E_{crane} + E_{pump} + E_{equipment} + E_{temporary} \quad (11)$$

$$I_{E,j} = E_{tot,CIS} / E_{tot,j} \quad (12)$$

2.6. Construction Efficiency Index – CEI

The three efficiency indicators are integrated into the proposed Construction Efficiency Index. The CIS system is used as the reference and therefore has CEI = 1.00. A PRE value above 1.00 indicates an integrated advantage under the adopted weighting system.

$$CEI_j = w_M I_{M,j} + w_E I_{E,j} + w_T I_{T,j} \quad (13)$$

$$w_M + w_E + w_T = 1 \quad (14)$$

$$CEI_j = 0.35 I_{M,j} + 0.35 I_{E,j} + 0.30 I_{T,j} \quad (15)$$

Table 2. CEI weighting scenarios

Scenario	w_M	w_E	w_T	Main priority
B	0.35	0.35	0.30	Balanced baseline
M	0.50	0.25	0.25	Material efficiency
E	0.25	0.50	0.25	Energy efficiency
T	0.25	0.25	0.50	Construction time

$$\Delta CEI = CEI_{\max} - CEI_{\min} \quad (16)$$

2.7. Break-Even Transportation Distance

The energy demand of the prefabricated alternative is expressed as a function of factory-to-site distance. The break-even distance occurs when the total energy demand of PRE becomes equal to that of CIS. The resulting value is project-specific and depends on the adopted system boundaries, component mass, transport-energy intensity and logistical correction factor.

$$E_{PRE}(d) = E_{PRE,0} + M_{PRE} e_{tr} \lambda d \quad (17)$$

$$E_{PRE}(d_{BE}) = E_{CIS} \quad (18)$$

$$d_{BE} = (E_{CIS} - E_{PRE,0}) / (M_{PRE} e_{tr} \lambda) \quad (19)$$

Transport-distance sensitivity is evaluated for 25, 50, 100, 150, 200 and 300 km, with recalculation of transportation

energy, total PRE energy, energy-efficiency indicator and CEI. This enables separate identification of the distance at which the pure energy advantage disappears and the distance at which the overall integrated CEI advantage disappears.

3. Results and Discussion

3.1. Definition of the Parametric Scenario

To evaluate the proposed methodology, a representative numerical scenario was defined for both construction systems. The selected values provide an internally consistent basis for comparative analysis. They represent modelling assumptions and not measured data from an executed building.

Table 3. Parametric input data for the comparative analysis

Parameter	CIS	PRE
Installed concrete volume (m ³)	1,850	1,750
Installed reinforcement mass (t)	215	225
Concrete material-loss rate (%)	5.0	2.0
Reinforcement material-loss rate (%)	3.0	1.0
Structural construction duration (days)	220	165
Additional production energy (GJ)	100	450
Fixed transportation energy (GJ)	450	150
Site energy (GJ)	850	300

The adopted material and transport assumptions were: concrete density $\rho_c = 2.4 \text{ t/m}^3$, unit energy factor for concrete $e_c = 0.95 \text{ MJ/kg}$, unit energy factor for reinforcing steel $e_s = 15.0 \text{ MJ/kg}$, transport-energy intensity $e_{tr} = 0.80 \text{ MJ/(t·km)}$, and logistics factor $\lambda = 1.20$. These values are used solely as parametric inputs and should be replaced or verified using a consistent project-specific life-cycle inventory dataset in a real application.

3.2. Material Consumption and Material Losses

Accounting for the assumed loss rates, the total structural-material resource input was calculated as approximately 4,895.3 t for CIS and 4,513.0 t for PRE. The prefabricated alternative therefore required approximately 7.8% less total structural-material input in the adopted scenario. The reduction was primarily associated with lower concrete volume and lower production losses, while PRE required a slightly higher reinforcement mass.

Table 4. Comparative material-efficiency results

Indicator	CIS	PRE
Gross concrete input (t)	4,673.7	4,285.7
Gross reinforcement input (t)	221.6	227.3
Total structural-material input (t)	4,895.3	4,513.0
Estimated material losses (t)	240.3	88.0
Overall loss ratio (%)	4.91	1.95
Material-efficiency indicator I_M	1.000	1.085

The calculated material-efficiency indicator for PRE was $I_M = 1.085$. This illustrates that improved material efficiency does not require every individual material quantity to decrease; rather, the final result depends on the combined balance of concrete, reinforcement and losses.

3.3. Construction-Time Efficiency

The structural construction duration was assumed to be 220 days for CIS and 165 days for PRE. This corresponds to a 25.0% reduction and a time-efficiency indicator of $I_T = 1.333$. The assumed time advantage reflects the possibility of overlapping factory production with site preparation and reducing repeated on-site formwork, reinforcement, casting and curing cycles. The result nevertheless depends on uninterrupted production, transport and assembly logistics.

3.4. Energy Comparison at the Reference Transport Distance

A factory-to-site transport distance of 50 km was adopted as the reference logistics scenario. At this distance, the calculated material-related energy was 7,764.7 GJ for CIS and 7,480.5 GJ for PRE. For a transported prefabricated-element mass of approximately 4,425 t, the variable transportation energy was 212.4 GJ. The resulting total energy demand was 9,164.7 GJ for CIS and 8,592.9 GJ for PRE.

Table 5. Energy-demand comparison at a 50 km transport distance

Energy component	CIS (GJ)	PRE (GJ)
Structural materials	7,764.7	7,480.5
Additional production	100.0	450.0
Transportation	450.0	362.4
Site activities	850.0	300.0
Total	9,164.7	8,592.9

At the reference distance, the PRE system exhibited approximately 6.2% lower total energy demand, corresponding to $I_E = 1.067$. The energy benefit results from the combined balance of lower material-related energy and substantially lower site energy, partly offset by higher factory-production energy.

3.5. Influence of Transportation Distance

The transport distance of prefabricated elements was varied between 25 and 300 km. The results show a continuous reduction in the isolated energy advantage of PRE as transportation distance increases. At 25 km the energy-efficiency indicator was 1.080, whereas at 300 km it decreased to 0.949, indicating that the prefabricated alternative became less favourable than CIS from the energy perspective alone.

Table 6. Influence of transport distance on PRE energy performance and CEI

Distance (km)	Variable transport energy (GJ)	Total PRE energy (GJ)	I_E	CEI_B
25	106.2	8,486.7	1.080	1.158
50	212.4	8,592.9	1.067	1.153
100	424.8	8,805.3	1.041	1.144
150	637.2	9,017.7	1.016	1.135
200	849.6	9,230.1	0.993	1.127
300	1,274.4	9,654.9	0.949	1.112

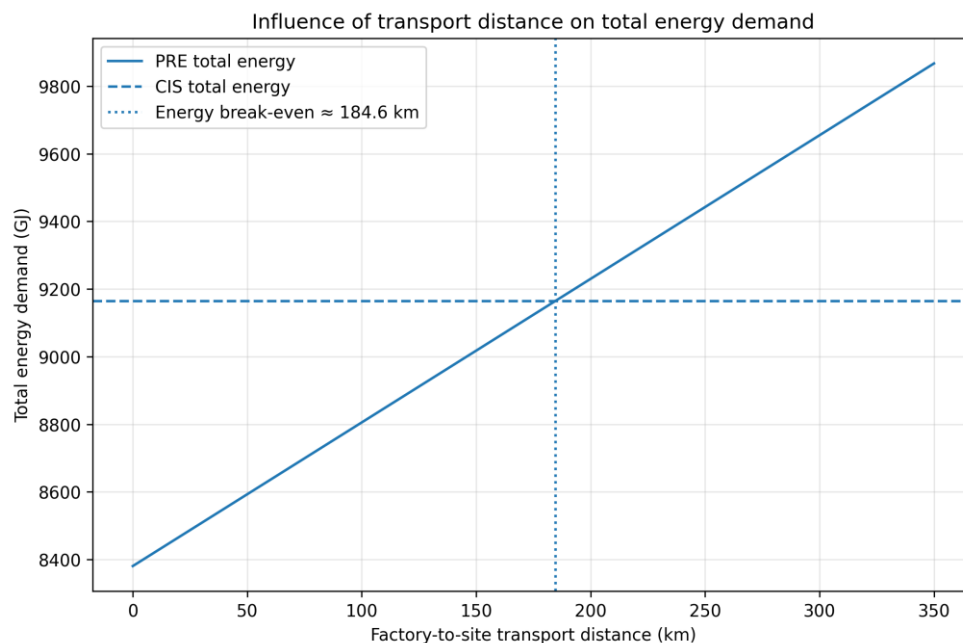


Figure 1. Influence of transport distance on total energy demand and the energy break-even point.

3.6. Break-Even Transportation Distance

The prefabricated-system energy demand excluding variable factory-to-site transport was $E_{PRE,0} = 8,380.5$ GJ. The energy increase per kilometre was 4.248 GJ/km. The resulting project-specific energy break-even transportation distance was approximately 184.6 km. Below this distance, PRE exhibits lower total energy demand than CIS under the adopted assumptions. Beyond this point, the additional transport burden causes total PRE energy demand to exceed that of the conventional alternative.

$$d_{energy, BE} \approx 184.6 \text{ km} \quad (20)$$

The calculated value is not a universal threshold for prefabricated construction. It is directly dependent on structural

configuration, transported mass, production system, vehicle performance, energy intensity and system boundaries. Its significance lies in demonstrating how logistics can be explicitly incorporated into technology selection.

3.7. Construction Efficiency Index at the Reference Distance

At 50 km, the three calculated efficiency indicators for PRE were $I_M = 1.085$, $I_E = 1.067$ and $I_T = 1.333$. Under the baseline weighting model, the resulting Construction Efficiency Index was $CEI_{PRE} = 1.153$, compared with $CEI_{CIS} = 1.000$. Thus, the prefabricated alternative exhibited an integrated efficiency advantage of approximately 15.3% in index terms. This difference should not be interpreted directly as an economic saving or life-cycle environmental reduction.

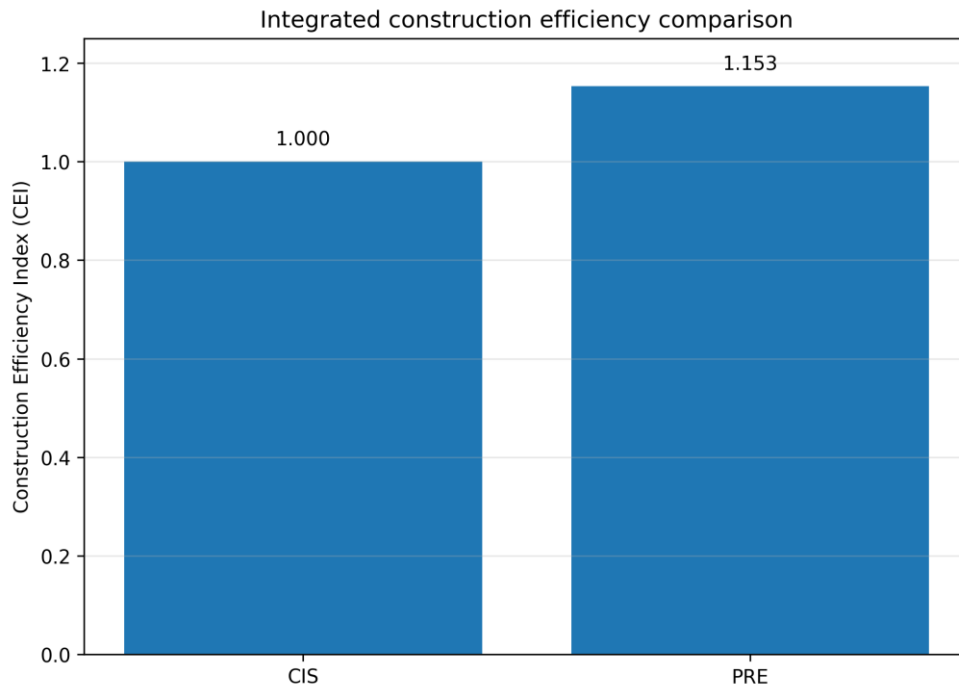


Figure 2. Integrated construction-efficiency comparison between CIS and PRE systems at the 50 km reference distance.

3.8. Sensitivity to Decision Priorities

Table 7. CEI sensitivity at the reference distance of 50 km

Weighting scenario	CEI – CIS	CEI – PRE
Balanced baseline – B	1.000	1.153
Material-oriented – M	1.000	1.142
Energy-oriented – E	1.000	1.138
Time-oriented – T	1.000	1.204

The prefabricated alternative remained preferable under all four weighting scenarios. The highest CEI was obtained for the time-oriented model, reflecting the strong relative advantage associated with construction duration. The variation between maximum and minimum PRE CEI values was $\Delta CEI = 0.066$, indicating that the system ranking remained relatively stable under the analysed decision priorities.

3.9. Energy Break-Even Versus Overall CEI Break-Even

An important result is that the energy break-even distance and the overall CEI break-even distance are not identical. The pure energy advantage disappears at approximately 185 km,

but PRE continues to achieve $CEI > 1.00$ because material and construction-time advantages remain. Under the baseline weighting model, the theoretical distance at which $CEI_{PRE} = CEI_{CIS}$ was approximately 1,454 km.

$$d_{energy, BE} \approx 185 \text{ km} < d_{CEI, BE} \approx 1454 \text{ km} \quad (21)$$

The very large theoretical CEI break-even value should be interpreted cautiously. Its significance is conceptual rather than prescriptive: a construction system can cease to be preferable according to one isolated criterion while still remaining favourable according to an integrated multi-criteria assessment.

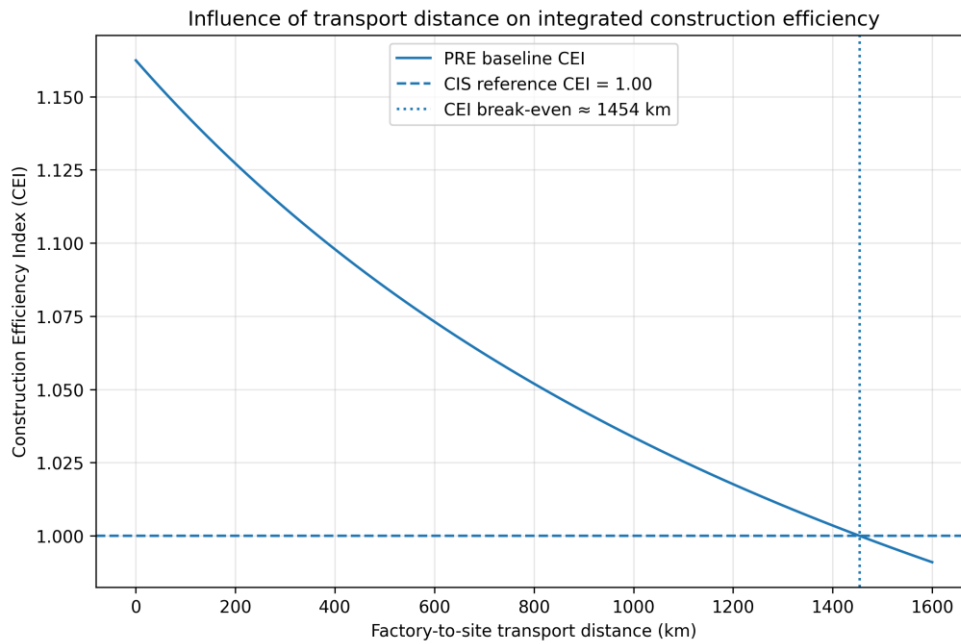


Figure 3. Influence of factory-to-site transport distance on the integrated Construction Efficiency Index.

3.10. Comparative Performance Summary

Table 8. Summary of comparative performance at a 50 km transport distance

Performance indicator	CIS	PRE	Relative PRE effect
Total material input (t)	4,895.3	4,513.0	−7.8%
Material losses (t)	240.3	88.0	Substantial reduction
Construction time (days)	220	165	−25.0%
Total energy demand (GJ)	9,164.7	8,592.9	−6.2%
I_M	1.000	1.085	PRE advantage
I_E	1.000	1.067	PRE advantage
I_T	1.000	1.333	PRE advantage
Baseline CEI	1.000	1.153	PRE advantage

Within the adopted scenario, construction-time efficiency represented the strongest relative advantage of prefabrication, followed by material efficiency and then the energy advantage. Transportation emerged as the principal variable capable of reversing the isolated energy ranking. The results therefore demonstrate that prefabricated construction should not be classified as universally superior or inferior to conventional cast-in-situ construction; its performance depends on the combined effects of structural design, material consumption, production efficiency, site productivity and logistics.

4. Conclusions

This study developed an integrated comparative methodology for evaluating the material, energy and construction-time efficiency of conventional cast-in-situ and prefabricated reinforced-concrete systems. A representative five-storey building with a gross floor area of approximately 5,000 m² was analysed through a clearly defined parametric numerical scenario.

The prefabricated system demonstrated higher material efficiency within the adopted assumptions. Total structural-material input decreased from approximately 4,895.3 t for CIS to 4,513.0 t for PRE, corresponding to a reduction of approximately 7.8%, while estimated material losses were substantially lower in the prefabricated scenario.

Construction-time efficiency represented the strongest comparative advantage of prefabrication. The structural construction duration decreased from 220 to 165 days,

corresponding to a 25% reduction and a time-efficiency indicator of $I_T = 1.333$.

At the reference transport distance of 50 km, the calculated total energy demand was approximately 9,164.7 GJ for CIS and 8,592.9 GJ for PRE. The energy advantage of approximately 6.2% was smaller than the time advantage and was strongly dependent on transportation distance.

The project-specific energy break-even transport distance was approximately 185 km. Below this distance, the prefabricated alternative exhibited lower total energy demand under the adopted assumptions; beyond this distance, the additional transport burden reversed the isolated energy ranking.

The proposed Construction Efficiency Index integrated material, energy and time performance. At the reference distance, $CEI_{CIS} = 1.000$ and $CEI_{PRE} = 1.153$. The prefabricated alternative remained preferable under balanced, material-oriented, energy-oriented and time-oriented weighting scenarios.

The energy break-even distance and integrated CEI break-even distance were substantially different. Although the isolated energy advantage disappeared at approximately 185 km, the overall CEI advantage persisted to a much larger theoretical distance because material and time benefits remained. This demonstrates the importance of multi-criteria assessment when individual indicators produce different conclusions.

The principal scientific contribution of the study is the combination of two decision-support elements: the dimensionless Construction Efficiency Index, $CEI = w_M I_M + w_E I_E + w_T I_T$, and the project-specific break-even transportation-

distance model, $d_{BE} = (E_{CIS} - E_{PRE,0}) / (M_{PRE} e_{tr} \lambda)$. Together they provide a transparent framework for analysing trade-offs between construction technologies.

A major limitation is that the numerical results are based on a parametrically defined reference building rather than measured data from a completed project. The adopted material quantities, loss rates, energy intensities, site-energy requirements and transport factors are modelling assumptions and should not be interpreted as universal values.

Future research should apply the methodology to completed reinforced-concrete projects using verified bills of quantities, construction schedules, factory-energy records, transport logs and project-specific life-cycle inventory data. The CEI framework may also be extended to incorporate cost, greenhouse-gas emissions, labour productivity, durability and end-of-life scenarios. The overall conclusion is that optimal construction-system selection is a function of materials, energy, time and logistics rather than a single universal claim of technological superiority.

References

- [1] Cheng, M., Huang, Z., & Zheng, Y. (2025). A review on life-cycle carbon emissions of reinforced concrete buildings: Calculation and reduction. *Journal of Cleaner Production*, 526, 146501. <https://doi.org/10.1016/j.jclepro.2025.146501>.
- [2] Zhou, F., Ning, Y., Guo, X., & Guo, S. (2023). Analyze Differences in Carbon Emissions from Traditional and Prefabricated Buildings Combining the Life Cycle. *Buildings*, 13(4), 874. <https://doi.org/10.3390/buildings13040874>.
- [3] Wang, H., Zhang, Y., Gao, W., & Kuroki, S. (2020). Life Cycle Environmental and Cost Performance of Prefabricated Buildings. *Sustainability*, 12(7), 2609. <https://doi.org/10.3390/su12072609>.
- [4] Abey, S. T., & Anand, K. B. (2019). Embodied Energy Comparison of Prefabricated and Conventional Building Construction. *Journal of The Institution of Engineers (India): Series A*, 100, 777–790. <https://doi.org/10.1007/s40030-019-00394-8>.
- [5] Mao, C., Shen, Q., Shen, L., & Tang, L. (2013). Comparative study of greenhouse gas emissions between off-site prefabrication and conventional construction methods: Two case studies of residential projects. *Energy and Buildings*, 66, 165–176. <https://doi.org/10.1016/j.enbuild.2013.07.033>.
- [6] Li, C. Z., Tam, V. W. Y., Lai, X., Zhou, Y., & Guo, S. (2024). Carbon footprint accounting of prefabricated buildings: A circular economy perspective. *Building and Environment*, 258, 111602. <https://doi.org/10.1016/j.buildenv.2024.111602>.

Intelligent Brazing Materials

Emilia Florina Binchiciu^{1*}, Ionelia Voiculescu², Florin Catalin Tabacu³, and Ioan Binchiciu⁴

¹ SC SUDOTIM AS SRL, 300222, M Viteazu no.30, Timișoara, Romania, sudotim@gmail.com

² National University of Science and Technology POLITEHNICA Bucharest, 060042, Splaiul Independenței 313, Bucharest, Romania.

³ SC LITE CORPORATION SRL, 300079, E. Ungureanu no.17, Timișoara, Romania.

⁴ SC SUDOTIM AS SRL, 300222, M Viteazu no.30, Timisoara, Romania.

ABSTRACT. The paper presents the research carried out for the development of brazing materials which, in a single pass, deposit two layers in the brazing joints: a buffer layer with high diffusion potential and increased silver content, and a filling layer with high strength and reduced silver content. The brazing performance of Ag20-type coated rods was improved by introducing a percentage of Ag40-type powder into the deoxidizing coating. The research was completed by establishing and patenting both the product formulation and the manufacturing process. The new product was successfully tested for producing brazed joints in copper pipes, copper-to-steel joints, and steel-to-tungsten carbide joints. The results of the mechanical tests met the required specifications, while the metallographic analysis of the joints showed an increase in diffusion of approximately 18.5% compared with the diffusion obtained using Ag20-type rods. The advantages of the brazing process using the new products consist of increased brazing productivity, improved quality of the brazed joints, and reduced environmental emissions from the resulting slag.

1. Introduction

The aim of the research is to develop coated rods for brazing with high efficiency and technological facilities for intelligent single-pass deposition of two layers, a buffer with high diffusion potential and rich in silver and a brazing joint filler with low silver content and high mechanical strength [1].

The new material [2] meets the technological condition, imposed for flame brazing and coated rods, of melting the deoxidizing coating before melting the metal rods, which allows increasing the deposition efficiency by introducing into the coating mass system, initially consisting of a mixture of deoxidizing substances, a portion of a metal alloy with melting temperatures at the level of the deoxidizing flux and high diffusion potential in the base materials.

The innovative principle, mentioned above, for obtaining coated rods for brazing with silver alloys with diffusion properties at the level of the Ag 40 type and mechanical strength of the Ag25 type. The experiments were carried out with materials that comply with environmental protection standards [3] and sustainable development principles for the circular economy [4].

2. Experiments

The experimental program was carried out in three main directions: improving the diffusion potential of the brazing material in the base materials; developing, optimizing and finalizing the product recipe and adapting and finalizing the coated rod manufacturing process to the new requirements for producing high-yield coated rods.

2.1 Improving diffusion potential

Previous research conducted by the authors highlighted the possibility of modifying the deposition yield by adding metal precursors to the deoxidizing coating, an idea also extended to increase the diffusion potential by adding metalloids, post-transition metals, non-metals with growth effect, the wetting and deoxidation properties of the melts which can be influenced from a structural point of view, after solidification by alloying and/or micro-alloying in the metal bath.

In order to determine how to influence the diffusion potential, a series of combinations of copper with zinc, silver, antimony, phosphorus, tin, carbon were performed, which were developed in the form of briquetted precursors (Fig. 1).

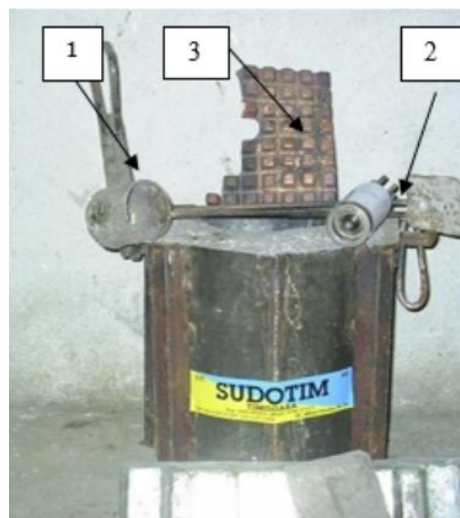


Fig.1. Charge melting stand with gas flame and compressed air.

1-Furnace crucible; 2-liquefied petroleum gas burner; 3-Briquette precursors.

The precursors were ground and introduced into the coating to determine the effects on brazing. An example is shown in Fig. 1b.

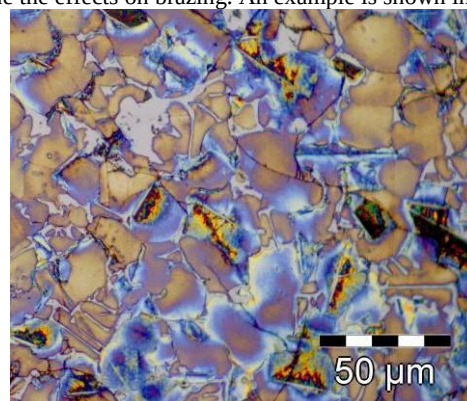


Fig.2. Microstructure of cast 85%Cu-5%P-10%Si alloy . Magnification 500x .

2.2 Development and finalization of the product recipe for VAg25SnSiPR coated rods

The aim was to produce reasonably priced coated rods for high-efficiency brazing of pipe-to-copper pipe and steel pipe-to-copper pipe joints. The product recipe optimized on the minimum cost, maximum diffusion criterion of the VAg25SnSiPR rods is presented in Table 1.

Table 1. Optimized product recipe of VIAg25SnSiPR rods.

Raw materials and materials	Participation in the product [% by mass]	Constituents [% by mass]
Naked rods SR EN ISO 17672:2010	65%	Ag125; $\Phi 2 \times 500 \text{ mm}$
Deoxidizing flux FH SR EN 1045:1999	25% powdery material, sort 0.15mm	35% boric frit (1/3 boric acid + 2/3 borax) 26% boric acid hydroxide 20% fluorite frit 19% binder+plasticizer
Activating precursors of the Cu-Sn-P-Si and Ag-Cu-Zn-Sn types	10% nanopowders	6%[Ag140/ENISO17672:2010] 4%[50%Cu-40%Sn-8%P-2%Si]

2.3 Development and implementation of the manufacturing process of VIAg25SnSiPR.

The introduction of metallic precursors ground in planetary mills into the coating modified the extrusion parameters of the coating mass on the rod, which led to a series of experiments to optimize and adapt the classic process of manufacturing extruded coated rods (Figure 2) to the new conditions.



Fig.3 . Manufacturing line rods WRAPPED for brazing .

The process parameters optimized on the minimum cost criterion are presented in Table 2.

Table 2. Parameters of the manufacturing process of VIAg25SnSiPR rods.

Process parameters	Optimized values
Dry homogenization time	8 ± 2 minutes
Wet homogenization time	6 ± 2 minutes
Briquetting pressure	20 ± 0.5 MPa
Extrusion pressure	20 ± 1 MPa
Rod mass flow rate	approx. 5.9 kg/hour
Coating mixture mass flow rate	approx. 2.5kg/hour
Wrapped rod take-up belt speed	approx. 9kg/hour

The problems of bare rod buckling, pressure jump extrusion and cracking of the coating were solved by modifying the rod feed train,

increasing the wet mixing temperature and controlling the humidity in the drying chamber.

The product recipe and the production process have been patented.

3. Results.

The production process presented above was used to produce a test batch, used to characterize the VIAg25SnSiPR product, in terms of deposition and technological performance.

3.1 Characterization of deposits with VIAg25SnSiPR rods.

The coated rods from the test batch were used to create, by melting with an oxyacetylene flame, a sample of deposited metal which was subjected, according to the regulations in force, to chemical analysis on a laboratory spectrometer, metallographic examination to highlight the microstructure and to hardness tests to confirm the structural analysis.

analysis was also performed on the bare rods under the same conditions, for comparison. The results are presented in Table 3.

Table 3 Chemical composition of MD and MV

Sample mark	Composition [% by mass]						
	Ag	Wt h	Zn	CD	Sn	An d	P
MV	24.	39.	31.	-/	1.5	-/	-/
Ag125 SR	0	0	0	0.01	...	-/-	0.0
EN ISO	...	...	...	0	2.5		08
17672/201	26.	41.	35.				
0	0	0	0				
prescribed							
Determine d MV	25.	40.	32.	0.00	1.8	0.1	0.0
	2	5	7	8		2	06
MD	25.	40.	31.	0.00	2.1	0.2	0.0
	6	7	2	7		5	2

Ag, Sn, and P additions are observed in the deposition (MD) compared to the composition of the rod (MV) which will be found in the bonding process in the buffer layer. The deposition defects and structural constituents were determined by metallographic analysis on the deposited metal sample, etched with ammoniacal cupric chloride, figure 3.



Fig. 3. a. MD microstructure [100X].

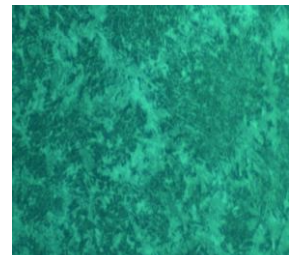


Fig. 3.b. MD microstructure [500X].

The metallographic analysis revealed a biphasic structure of alpha and beta solid solutions without defects such as micro cracks or imperfections such as hydrogen diseases and/or oxygen pores. The metallographic analysis was accompanied by sclerometric tests which revealed an average VICKERS-HV _{0.1} hardness of 184.6, confirming the observed structure.

3.2 Checking the brazing behavior

The brazing behavior was verified under industrial conditions, practically during the manufacture of refrigeration installations, through 2 concrete cases of joining: copper pipe to copper pipe and steel pipe to copper pipe, in capillary joints. The joints presented above were made until the date of the experiments with Ag40 type alloys, which are replaced by the new product. The 2 types of joints,

in batches of 24 pieces for each type, were made by oxyacetylene brazing with neutral flame with VIAg25SnSiPR rods. The batches thus obtained were subjected to pressure testing, in accordance with the regulations in force, without pressure losses or material deformations. The longitudinal cross-section investigation of the joints, figure 4, revealed for all joints a complete penetration and diffusion of the brazing alloy into the brazing materials at the level of the alloys with 40% Ag, probably determined by the silver content in the buffer layer.



a. b.
Fig. 4. Steel pipe joint design in copper pipe .
a) joint design ; b) joint design

Figure 5 shows the critical case of the steel pipe to copper pipe joint. , The microscopic examination was performed according to SR 5000-97 and STAS 5500-74 . The structural analysis was performed on the MeF2 optical microscope, at 100X.

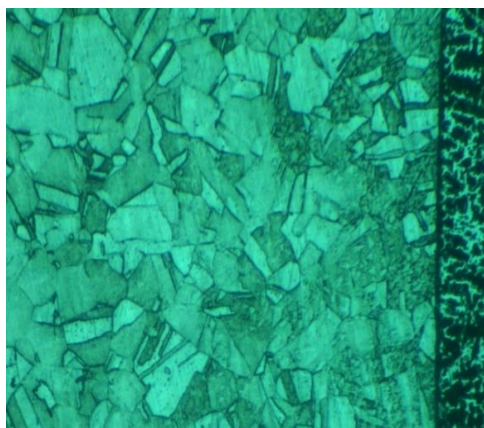


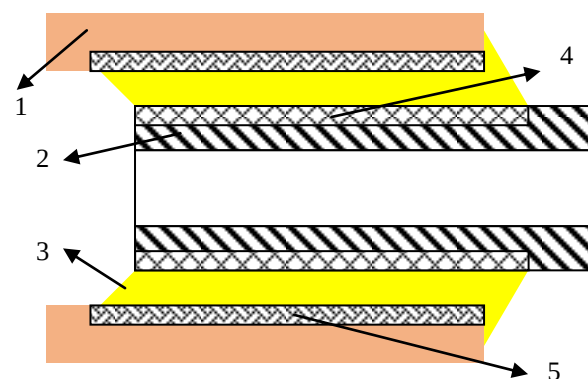
Fig. 5. [E1 attack , 100X].

The test joints were subjected to tensile rupture testing and the results were in accordance with the requirements, all tested samples either ruptured in the base material Figure 6.

The high strength of the joints is explained by the design of the figure 7.



Fig. 6. Tensile test specimen for steel pipe-to-copper pipe joint.



b)
Fig.7. Test batch of joints. a) samples made; b) brazed assembly
1-MB1(copper,brass); 2-MB2(steel);3-soldering alloy; 4-ZIT MB2; 5-ZIT MB1

Conclusions

The research conducted was completed with the following results:

- a method for obtaining coated rods for brazing with high efficiency and deposition of 2 layers in a single pass was presented and experimented.

- a new generation of coated rods for brazing was created, by equipping the coating with adjuvant metallic systems and/or process catalysts, VIAg25SnSiPR.

- the classic manufacturing line of coated rods for brazing was adapted to the conditions of equipping the deoxidizing coating with metallic systems.

- the product recipe of the new generation of smart brazing materials has been patented.

- two high-efficiency and reasonably priced brazing technologies were developed, characterized and qualified according to SR EN13134:2002.

- the idea listed in the preamble has been confirmed through experimental research and AI-assisted simulation.

Bibliography

1. E.F. Binchiciu, Materials with advanced precursors and brazing technologies "Politehnica" University Timisoara Faculty: Industrial Engineering – **Ph.D.** no. 6122/20.12.2016 *Industrial engineering*, (2016).
- 2.E.F. Binchiciu, I. Voiculescu, V. Geantă, A. Binchiciu, R. Stefănoiu, T.D. Tihanov. Coated rods for brazing and its manufacturing process, Patent of invention RO132041 B1 (2019).
- 3.REACH EC Regulation no. 1907/2006, review 2013, European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals - REACH.

4.www.weldfy.eu; <https://lms.weldify.eu/>

Innovative Nanomaterials for the Conservation and Sustainable Protection of Cultural Heritage

Iskra Tsvetanska, Ivanka Yankova, Kamelia Nucheva
University of Library Studies and Information Technologies - Sofia, Bulgaria,
i.cvetanska@unibit.bg, i.yankova@unibit.bg, nucheva@unibit.bg

Abstract: Cultural heritage objects represent an essential component of human identity, history, and collective memory. However, monuments, artworks, manuscripts, archaeological artefacts, and historical buildings are continuously exposed to environmental deterioration processes, including humidity fluctuations, pollution, biological colonization, salt crystallization, and mechanical degradation. Conventional conservation methods often provide effective protection but may involve invasive procedures, limited durability, or the use of environmentally harmful chemicals. In recent decades, nanotechnology has emerged as a promising approach for sustainable conservation due to the unique physicochemical properties of nanomaterials, including high surface area, enhanced reactivity, photocatalytic activity, and the possibility of designing multifunctional protective coatings. This review discusses innovative nanomaterials used in cultural heritage conservation, including silica nanoparticles, titanium dioxide, zinc oxide, calcium hydroxide nanoparticles, graphene-based materials, and nanocomposites. Their applications in consolidation, cleaning, protection against pollutants, antimicrobial treatments, and sustainable preservation strategies are examined.

The report is under project No. KII-06-H90/6 dated 10.12.2024 on the topic: "Ecologically sustainable conservation strategy for written heritage" from the Scientific Research Fund, Competition for funding of fundamental scientific research - 2024. Supervised by Chief Associate Professor, PhD, MSc Eng. Iskra Tsvetanska.

KEYWORDS: NANOMATERIALS; CULTURAL HERITAGE CONSERVATION; NANOPARTICLES; PROTECTIVE COATINGS; SUSTAINABLE RESTORATION; NANOTECHNOLOGY.

1. Introduction

The preservation of cultural heritage is a multidisciplinary challenge involving chemistry, materials science, conservation science, and environmental engineering. Historical materials such as stone, ceramics, paper, wood, metals, and wall paintings undergo progressive deterioration due to interactions with atmospheric pollutants, moisture, microorganisms, and human activity. [4] Climate change has further intensified these challenges by increasing temperature variations, humidity instability, and the frequency of extreme weather events affecting heritage sites worldwide. [12]

Traditional conservation approaches have relied on organic polymers, inorganic consolidants, and chemical cleaning agents. Although many of these materials have demonstrated effectiveness, they can suffer from problems such as incompatibility with original substrates, ageing, poor reversibility, and environmental toxicity. [1] Consequently, there is growing interest in developing sustainable conservation technologies capable of providing long-term protection while minimizing damage to cultural objects.

Nanotechnology offers new possibilities by exploiting materials with dimensions typically below 100 nm. At this scale, materials exhibit unique optical, mechanical, chemical, and biological properties that differ significantly from their bulk counterparts. [11] Nanomaterials can penetrate porous structures, enhance mechanical stability, control chemical reactions, and provide protective functionalities such as self-cleaning or antimicrobial activity. [3]

2. Role of Nanotechnology in Cultural Heritage Conservation

Nanotechnology has introduced innovative solutions for several major conservation problems:

- consolidation of fragile materials;
- removal of unwanted deposits and pollutants;
- protection against water infiltration;
- inhibition of microbial growth;

- development of environmentally friendly protective coatings.

The effectiveness of nanomaterials is mainly related to their high surface-to-volume ratio, which increases chemical interaction with heritage substrates. Furthermore, nanoscale engineering allows researchers to tailor particle size, morphology, surface functionality, and compatibility with specific historical materials. [7]

One of the major advantages of nanotechnology is the possibility of creating multifunctional materials. For example, a single nanocomposite coating may simultaneously provide hydrophobic protection, UV resistance, and antimicrobial properties, reducing the need for repeated restoration interventions.

3. Silica Nanoparticles for Consolidation and Protection

Silica nanoparticles (SiO_2) are among the most widely investigated nanomaterials for cultural heritage conservation because of their chemical stability, transparency, and compatibility with mineral substrates. They are particularly useful for consolidating deteriorated stone materials, especially limestone and sandstone.

The consolidation mechanism is based on the penetration of nanosilica dispersions into porous structures, followed by gel formation and strengthening of weakened regions. Compared with traditional silica-based consolidants, nanosilica offers deeper penetration and better control over the treatment process. [14]

Studies have demonstrated that silica nanoparticles can improve mechanical strength without significantly altering the appearance or permeability of stone surfaces. [9] This is particularly important because conservation treatments must preserve the original aesthetic and physical characteristics of historical materials.

However, challenges remain regarding aggregation of nanoparticles, long-term stability, and optimization of particle size distribution. Surface modification of silica nanoparticles with organic or inorganic functional groups has been proposed to improve compatibility and performance. [7]

4. Titanium Dioxide Nanoparticles and Photocatalytic Conservation

Titanium dioxide nanoparticles (TiO_2) have attracted considerable attention due to their photocatalytic activity, chemical stability, low toxicity, and relatively low cost. Under ultraviolet

radiation, TiO_2 generates reactive oxygen species capable of decomposing organic pollutants, including atmospheric contaminants and biological residues. [6]

In cultural heritage conservation, TiO_2 coatings have been investigated for self-cleaning surfaces on architectural monuments. Their photocatalytic properties allow the degradation of organic pollutants such as hydrocarbons deposited from urban pollution. [8]

Additionally, TiO_2 nanoparticles exhibit antimicrobial properties by producing oxidative stress that can damage bacterial and fungal cells. This makes them attractive for protecting stone monuments and historical surfaces affected by biological colonization.

Despite these advantages, TiO_2 applications require careful evaluation because excessive photocatalytic activity may potentially accelerate degradation of organic components in artworks, particularly pigments and binders. Therefore, controlled formulations and protective strategies are necessary.

5. Zinc Oxide Nanoparticles in Heritage Protection

Zinc oxide nanoparticles (ZnO) represent another important class of functional nanomaterials used in conservation. ZnO possesses antimicrobial activity, UV absorption capability, and photocatalytic properties.

The antimicrobial effect of ZnO nanoparticles results from the generation of reactive oxygen species and the release of zinc ions, which interfere with microbial metabolism. [13] These properties make ZnO suitable for applications in protecting paper, textiles, wood, and stone materials.

Furthermore, ZnO -based coatings can provide UV shielding, reducing photo degradation of sensitive historical materials. However, possible interactions between ZnO nanoparticles and pigments require detailed assessment before practical application.

6. Calcium Hydroxide Nanoparticles for Lime-Based Materials

Calcium hydroxide nanoparticles ($\text{Ca}(\text{OH})_2$ nanoparticles) have become one of the most successful examples of nanotechnology applied to cultural heritage conservation.

Traditional limewater treatments have historically been used for consolidating carbonate-based materials. However, their effectiveness is limited because calcium hydroxide has low solubility and poor penetration ability. Nanocalcium hydroxide overcomes these limitations due to its extremely small particle size and increased reactivity. [2]

After application, nanoparticles penetrate cracks and porous structures, reacting with atmospheric carbon dioxide to form calcium carbonate, which restores cohesion within deteriorated limestone, frescoes, and lime-based mortars.

Nanocalcium hydroxide has been successfully applied in the conservation of wall paintings and architectural surfaces because it provides chemical compatibility with original carbonate materials while minimizing visual alteration. [7]

7. Titanium Dioxide Nanoparticles and Photocatalytic Conservation

Graphene and graphene oxide have emerged as advanced materials with exceptional mechanical strength, electrical conductivity, and barrier properties. Their application in cultural heritage conservation is still developing but shows significant potential.

Graphene-based coatings may provide protection against moisture, oxygen diffusion, and chemical pollutants due to their highly impermeable structure. [10] Additionally, graphene oxide can be functionalized with nanoparticles to create hybrid materials with enhanced antibacterial or protective properties.

Nanocomposites combining graphene derivatives with silica, titanium dioxide, or metal nanoparticles represent a promising direction for developing multifunctional conservation materials.

8. Environmental Sustainability and Future Perspectives

The development of sustainable conservation technologies requires balancing effectiveness, safety, and environmental impact. Nanomaterials contribute to sustainability by enabling:

- longer-lasting protective treatments;
- reduced frequency of restoration interventions;
- lower consumption of chemical cleaning agents;
- minimally invasive conservation procedures.

Nevertheless, potential risks associated with nanoparticle release, toxicity, and environmental accumulation must be carefully evaluated. Future research should focus on green synthesis methods, biodegradable nanomaterials, and comprehensive life-cycle assessments. [5]

The integration of nanotechnology with digital monitoring systems, artificial intelligence, and advanced characterization techniques may further improve preventive conservation strategies.

9. Conclusion

Innovative nanomaterials represent a transformative approach for the sustainable conservation of cultural heritage. Materials such as silica nanoparticles, TiO_2 , ZnO , calcium hydroxide nanoparticles, and graphene-based nanocomposites provide new opportunities for consolidation, protection, cleaning, and antimicrobial treatment of historical materials.

Although significant progress has been achieved, responsible implementation requires careful evaluation of compatibility, durability, and environmental safety. Future developments in green nanotechnology are expected to provide increasingly efficient and sustainable solutions for preserving cultural heritage for future generations.

10. References

1. Baglioni, P., & Chelazzi, D. (2013). *Nanoscience for the Conservation of Works of Art*. Royal Society of Chemistry.
2. Baglioni, P., Giorgi, R., & Chelazzi, D. (2012). Nanotechnologies in the conservation of cultural heritage. *Journal of Cultural Heritage*, 13, S1–S5.
3. Baglioni, P., Bonelli, N., Chelazzi, D., et al. (2015). Sustainable materials and nanotechnology for cultural heritage conservation. *Chemical Society Reviews*, 44, 5419–5431.
4. Cappitelli, F., & Sorlini, C. (2008). Microorganisms attack synthetic polymers in items representing our cultural heritage. *Applied and Environmental Microbiology*, 74, 564–569.

5. Fadeel, B., Farcas, L., Hardy, B., et al. (2018). Advanced tools for the safety assessment of nanomaterials. *Nature Nanotechnology*, 13, 537–543.
6. Fujishima, A., Zhang, X., & Tryk, D. A. (2008). TiO₂ photocatalysis and related surface phenomena. *Surface Science Reports*, 63, 515–582.
7. Giorgi, R., Baglioni, M., Berti, D., & Baglioni, P. (2010). New methodologies for the conservation of cultural heritage using nanotechnology. *Accounts of Chemical Research*, 43, 695–704.
8. La Russa, M. F., Ruffolo, S. A., Barone, G., et al. (2016). Nanotechnologies for cultural heritage conservation. *Applied Physics A*, 122, 385.
9. Mosquera, M. J., Pinho, L., & Facio, D. S. (2010). New nanomaterials for conservation of stone materials. *Journal of Cultural Heritage*, 11, 123–128.
10. Novoselov, K. S., Fal'ko, V. I., Colombo, L., et al. (2012). A roadmap for graphene. *Nature*, 490, 192–200.
11. Poole, C. P., & Owens, F. J. (2003). *Introduction to Nanotechnology*. Wiley.
12. Sesana, E., Gagnon, A. S., Bertolin, C., & Hughes, J. (2021). Adapting cultural heritage to climate change risks. *Climate Risk Management*, 31, 100249.
13. Sirelkhatim, A., Mahmud, S., Seeni, A., et al. (2015). Review on zinc oxide nanoparticles: antibacterial activity and toxicity mechanism. *Nano-Micro Letters*, 7, 219–242.
14. Ziegenbalg, G., Brümmer, F., & Schubert, U. (2010). Nanomaterials for conservation of stone. *Materials Research Society Symposium Proceedings*, 1319, 1–8.

Thermodynamic Properties and Phase Equilibria in the Fe–W–C System

Vladyslav Kaverynskyi¹, Stepan Kyrlyuk¹, Gennadii Bagliuk¹
Yevheniia Kyrlyuk¹, Volodymyr Kudin², Larysa Romanova¹, Valentyna Sudavtsova¹,
Frantsevi Institute for Problems in Materials Science, NASU, Kyiv, Ukraine¹
Taras Shevchenko National University of Kyiv, Kyiv, Ukraine²
hisie@ukr.net

Abstract: By utilizing the tools of the PyCALPHAD library and a thermodynamic database, Python-based software components were developed to calculate the energetic characteristics of phase transitions, enabling the prediction of Fe–W–C system behavior under varying composition and temperature. According to the CALPHAD calculation, it was established that within the temperature range of 500–2000 K for the composition of 43 at.% Fe, 43 at.% W, and 14 at.% C, an intermediate Fe₃W₃C phase is formed, which melts incongruently at 1770 K.

Keywords: THERMODYNAMICS, CALPHAD, Fe-W-C SYSTEM, PHASE EQUILIBRIUM, THERMODYNAMIC PROPERTIES

1. Introduction

Iron-based alloys are widely used in various fields of science and technology. The quality of products made from them depends on the methods of production, which can be improved based on physicochemical properties. Steel matrix composites are formed by adding reinforcing materials (such as nitrides, carbides, borides, oxides and intermetallics) to the steel matrix, which allows the production of materials with improved performance characteristics [1–5]. The synthesis of such composites is an effective approach to improve the mechanical properties of steel: strength, hardness, durability and wear resistance [4]. Tungsten carbide (WC) is a common ceramic material that is widely used as an agent in nickel- and iron-based alloys [6]. WC is well suited for such materials due to its high melting point, thermal stability, strength and hardness, good wettability and thermal expansion coefficient similar to iron.

Since most methods of producing steels and alloys are associated with their melting, the thermodynamic properties of iron alloys in the liquid state are of great importance. Studies of phase equilibria are key to understanding the behavior of materials and alloys at high temperatures. At the same time, the determination of the liquidus and solidus surfaces in a wide concentration range is of great importance for the development of new alloys and the optimization of existing technologies. Experimental work remains one of the main research methods in this area at present. But studies of the thermodynamic properties of melts and phase equilibria in alloys of the Fe–W–C system have not been conducted at present. Given the complexity of high-temperature experiments to determine the thermodynamic properties of melts, it is advisable to calculate them from similar data for limit binary systems according to the “analytical” Redlich–Kister–Mujian model. Therefore, we will consider and analyze the thermodynamic properties of melts of limit binary subsystems first.

2. Results and discussion

Fe–W system. Thermochemical properties of iron-tungsten melts were determined by calorimetry [7–10]. The results of these works are compared in Fig. 1 and given in Table 1.

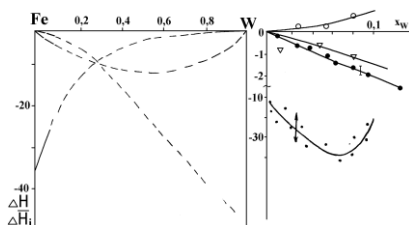


Fig. 1 Enthalpies of mixing of melts of the system:

— [7], 1873 K
- - [8], 1863 K;
... [9], 1960 K

It can be seen that there is a very good agreement between the data of [8–10], and [7] do not coincide with them even in sign. This discrepancy is difficult to explain, since the results of the mixing enthalpies of the binary systems Fe–Cr(V, Ta, Mo, Nb) of [7] agree with the data of other studies. But since the data of three independent studies of Fe–W melts [8–10] coincide, it can be stated that they correctly reflect the energy of interparticle interaction in melts of the Fe–W system.

Table 1: Thermochemical properties of melts of the Fe–W system, in kJ/mol.

x W	-ΔH [9] T=1960 K	-ΔH _W	-ΔH [9] T=1960 K	-ΔH [8] T=1863 K	x W	ΔH [7] T=1873 K
0	0	10±1	0	0	0.05	0.42
0.02	0.25±0.05	22±2	0.35±0.05	0.2	0.02 5	0.38
0.04	0.6±0.05	31±3	0.7±0.05	0.5	0.07 5	0.8
0.06	1.0±0.1	35±3	1.1±0.1	0.8		
0.08	1.6±0.1	36±3	1.7±0.1	1.1		
0.10	2.0±0.2	27±3	2.1±0.2			
0.11	2.4±0.2	20±2	2.5±0.2			

The EMF method in the concentration range 0.95 < x_{Fe} < 1.0 at 1870 K investigated [11] the activities of tungsten in liquid alloys of the Fe–W system using a concentration chain of the form:

W–WO₂/ZrO₂–Y₂O₃/ Fe–W, WO₂.

The obtained EMF values and the calculated tungsten activities in melts of the iron-tungsten system at 1870 K are given below.

Table 2: Values of calculated EMF

x W	E 10 ³ , B	a _{w(sp.)}	a _{w(lp.)}
0,068	70,8	0,1724	0,1711
0,0188	58,9	0,2317	0,2270
0,0298	44,5	0,3313	0,3208
0,03541	32,1	0,4507	0,4338

It was found that the tungsten activities of alloys of the Fe–W system are characterized by very large positive deviations from Raoult's law and correlate with the data [12].

Fe–C system. Thermodynamic data of melts of this system have been studied in many works, since iron-carbon alloys are very important for the development of ferrous metallurgy. The enthalpies of mixing and dissolution of melts of the Fe–C system have been determined at 1873 K and 1973 K [13,14], and the activities of the components - [15, 16]. The most reliable thermodynamic properties at 1900 K of Fe–C melts are given in Table. 3.

W–C system. W and C form the compounds WC and W₂C, and their enthalpies of formation (ΔH_f) are determined to be: – 38 and – 46 kJ/mol. However, the thermochemical properties of melts of the W–C system have not been investigated, so we have taken them equal to the enthalpies of formation. Using the molar enthalpies of melts of binary boundary systems, similar data were calculated for ternary melts of the Fe–W–C system according to the “analytical” Redlich–Kister–Mujianu model (Fig. 2). It can be seen that the extreme value of the integral molar enthalpy of melts of this ternary system is –46 kJ/mol and falls on the W_{0.66}C_{0.34} melt, i.e. the main contribution to the interaction energy between dissimilar atoms of these ternary melts is made by the boundary W–C system.

Table 3: Thermodynamic properties of Fe-C melts (standard state - liquid iron and liquid supercooled carbon) at 1900 K

x_C	$-\Delta_m \bar{H}_C$	$-\Delta_m H$	$\Delta_m \bar{S}_C^{exc.}$	$-\Delta_m S^{exc.}$	$\Delta_m \bar{G}_C^{exc.}$	$-\Delta_m G^{exc.}$
	kJ/mol		J/(mol·K)		kJ/mol	
0	83,3±15,1	0	-	0	57,7±13,4	0
0,02	67,2	1,5	-6,9	0,2	54,0	1,1
0,04	59,9	2,7	-5,0	0,03	50,4	2,2
0,06	58,2±15,3	3,9±0,9	-6,0±4,0	0,4±0,1	46,8±13,5	3,1±0,9
0,08	59,4	5,1	-8,4	0,6	43,4	4,0
0,10	61,4	6,3	-11,2	0,8	40,2	4,8
0,12	62,2±15,7	7,5±1,8	-13,2±4,5	1,0±0,4	37,1±13,4	5,6±1,7
0,14	60,1	8,7	-13,6	1,3	34,2	6,3
0,16	53,8	9,9	-11,7	1,6	31,5	6,9

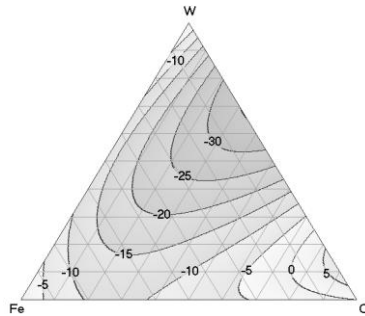


Fig. 2. Isoenthalpies of mixing of melts of the Fe-W-C system, calculated using the "analytical" Redlich-Kister-Mujianu model

Studies of phase equilibria are key to understanding the behavior of materials and alloys at different temperatures. However, despite their significant applied importance, the liquidus and solidus surfaces of the Fe-W-C system have not been studied due to the very high smelting temperatures of both Fe, W, C, and their compounds. Therefore, thermodynamic modeling is an important tool for studying such phase diagrams. An important aspect is the modeling of the energy characteristics of phase transitions, which allows predicting the behavior of systems when changing composition and temperature. To calculate the liquidus and solidus surfaces (including multidimensional ones), software components were created in Python, using the PyCALPHAD library tools and thermodynamic databases. According to CALPHAD calculations of phase equilibria in the temperature range of 500–2000 K for the composition 43% Fe 43% W, 14% C (at.%), an intermediate phase Fe_3W_3C is formed, which melts incongruently at 1770 K. The images of the liquidus and solidus projections of the Fe-W-C system obtained from the calculation data are shown in Figure 3.

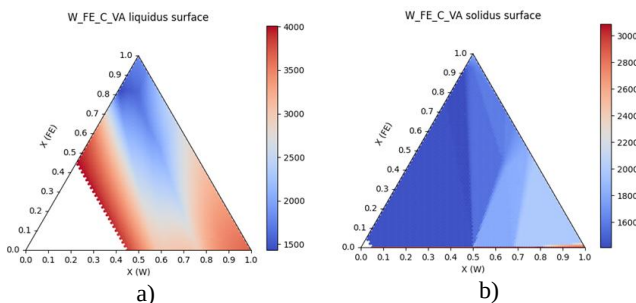


Fig. 3. Projections of the liquidus and solidus surfaces of the Fe-W-C system according to CALPHAD calculations: a) liquidus; b) solidus

On the liquidus surface, the W-C-enriched region has clear eutectic depressions and maxima due to the formation of stable tungsten carbides. Approaching the iron angle smoothes these features, signaling a transition to iron-based crystallization, and a zone of reduced liquidus temperatures extends inward from the Fe

angle. In this case, the Fe_3W_3C compound melts incongruently and affects the topology indirectly through adjacent phase equilibria. The solidus surface is relatively smooth in the carbon-rich corner, but along the W-Fe direction it has steps and discontinuities, successive solid-phase transformations involving carbide phases.

3. References

1. Bhowmik, A.; Kumar, R.; Beemkumar, N.; Kumar, A.V.; Singh, G.; Kulshreshta, A.; Mann, V.S.; Johnson Santhosh, A. Casting of particle reinforced metal matrix composite by liquid state fabrication method: A review. *Results Eng.* 2024, 24, 103152.
2. Kumar Yadav Nartu, M.S.K.; Agrawal, P. Additive manufacturing of metal matrix composites. *Mater. Des.* 2025
3. Tjong, S.C. Recent progress in the development and properties of novel metal matrix nanocomposites reinforced with carbon nanotubes and graphene nanosheets. *Mater. Sci. Eng. R Rep.* 2013, 74, 281–350.
4. Radhamani, A.V.; Lau, H.C.; Ramakrishna, S. CNT-reinforced metal and steel nanocomposites: A comprehensive assessment of progress and future directions. *Compos. Part A Appl. Sci. Manuf.* 2018, 114, 170–187.
5. AlMangour, B.; Grzesiak, D.; Yang, J.-M. Selective laser melting of TiC reinforced 316L stainless steel matrix nanocomposites: Influence of starting TiC particle size and volume content. *Mater. Dec.* 2016, 104, 141–151.
6. Enrici, T.M.; Dedry, O.; Boschini, F.; Tchuindjang, J.T.; Mertens, A. Microstructural and thermal characterization of 316L+WC composite coatings obtained by laser cladding. *Adv. Eng. Mater.* 2020, 22, 2000291.
7. Iguchi J., Nobori Sh., Saito K., Fuma T. Calorimetric Study of Heats of Mixing of Liquid Iron Alloys Fe-Cr, Fe-Mo, Fe-W, Fe-Nb, Fe-Ta // *J. Iron and Steel Inst. Jap.* - 1982. - Vol. 68, No. 6.
8. Naboru Yochiro Saito Ken, Iguta Yasutaka, Fukai Hiroa. Determination of heat of mixing of liquid iron with refractory metals // *Tetsu to Hagane.* - 1976. - Vol. 62, No. 1. - P. 558.
9. Sudavtsova B.C., Kurach V.P., Maryanchyk N.N., Batalyn G.I. Thermodynamic properties of double alloys of Fe-Ta, Fe-W systems // *Izv. Academy of Sciences of the USSR. Metals.* - 1989. - No. 6.
10. Sudavtsova V.S., Vovkotrub N.E., Kudin V.G. Thermodynamic properties of melts of binary systems Fe-Nb (Ta, W), Fe-Nb (Ta, W)-Al // *Metally.* - 2001. - No. 2. - P. 18–20.
11. Sudavtsova V.S., Vovkotrub N.E., Kudin V.G. Thermodynamic properties of liquid alloys of the iron-tungsten system // *Powder metallurgy.* - 2001. - No. 9/10. - pp. 86–89.
12. Ueshima Yoshiyuki The study of the thermodynamic properties of Fe-W alloys by Means of Knudsen cell with Mass Spectrometry // *J. Iron and Steel Inst. Jap.* - 1981. - V. 67. - No.12. - P.825.
13. Ichise E., Ueshima Y. Reexamination of the High Temperature Region of Fe-W Binary Alloys Phase Diagram // *J. Iron and Steel Inst. Jap.* - 1986. - V. 72. - No. 7. - P.791–798.
14. Elliot D.F., Glaizer M., Ramakrishna V. Thermochemistry of steelmaking processes. M.: Metallurgy, 1969; 252 p.
15. Mori T., Fujimura T., Okajima H., Yamauchi A. A effect of chromium, copper and tin on the activity of carbon in high carbon liquid steel // *J. Iron Steel Inst. Jpn.* - 1968. - V. 54. - P. 321–329.
16. Shenk H., Steinmeltz E., Glos M. Die thermodynamischen Eigenschaften des Systems Eisen-Kohlenstoff an der rihlenstoffreichen Seite des Systems // *Arch. Eisenhüttenwes.* - 1971. - V. 42. - P. 307–310.